Supporting Information for:

Dendritic and Linear Macromolecular Architectures for Photovoltaics – A Photoinduced Charge Transfer Investigation

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Experimental Section:

¹H-NMR spectra were recorded on a 400 MHz NMR spectrometer using the residual proton resonance of the solvent as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given, the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; d of d, doublet of doublet; m, multiplet, br, broad. ¹³C-NMR spectra were proton decoupled and recorded on a 100 MHz NMR spectrometer using the carbon signal of deuterated solvent as the internal standard. Mass spectrometry was performed on the Bruker Daltonics Reflex III (MALDI-ToF). UV-Visible spectra were obtained using a Cary 100 spectrophotometer and fluorescence data were collected using JASCO FP-6500 spectrofluorimeter. The molecular weights of the polymer and dendron-rod-coils were determined by size exclusion chromatography on a single injector mode GPC, using THF as eluent and toluene as the internal reference; either PMMA or PS standard was used for calibration and output was received and analyzed using a RI detector. Flash chromatography was performed with 37-75 μ m silica gel. Analytical thin layer chromatography was performed on silica plates with F-254 indicator and the visualization was accomplished by a UV lamp. THF and toluene were distilled over Na/Ph₂CO ketyl. Benzthiadiazole derivative has been synthesized and published earlier by our group.¹ Frechet-type dendrons² were synthesized according to reported

procedures. All other chemicals were obtained from commercial sources and used without any purification unless otherwise stated.

1. General procedure for conversion of alcohols to bromides (I):

The appropriate benzyl alcohol (1 equiv) and dimethylaminopyridine, DMAP (0.05 equiv) were dissolved in THF and the solution was cooled to 0 °C under argon atmosphere. Triethylamine (2.5 equiv) and mesyl chloride (2 equiv) were added dropwise, and allowed to stir at room temperature for 3 h. Upon completion of reaction, water was added and the compound was extracted with dichloromethane. The organic layer was concentrated under reduced pressure to afford crude mixture which was taken for further step without any purification.

To the above crude mixture in THF, LiBr (3-6 equiv) was added and the contents were allowed to reflux overnight. After completion of the reaction, the reaction mixture was partitioned between water and dichloromethane. The aqueous layer was extracted twice with dichloromethane and the organic layer was dried over Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by column chromatography using dichloromethane/hexane as the eluent.

2. General procedure for benzyl ether synthesis using phenol and alkyl halides (II):

A mixture of phenol (1 equiv), appropriate bromomethyl compound (1-1.2 equiv), dry K₂CO₃ (3-6 equiv), and 18-crown-6 (0.1 equiv) in THF was heated to reflux temperature and stirred vigorously under argon for 12h. The reaction mixture was allowed to cool to room temperature and solvent was evaporated to dryness. The residue was partitioned between water and dichloromethane. The organic layer was separated and aqueous layer was extracted with dichloromethane. The combined organic layer was dried over Na₂SO₄ and evaporated to dryness. The crude product was purified by column chromatography.

3. General procedure for conversion of aldehydes to alcohols (III):

To a stirring solution of appropriate aldehyde (1 equiv) in THF/methanol solvent mixture, sodium borohydride (2-3 equiv) was added in portions with efficient stirring. After the addition was complete the mixture was allowed to stir overnight. The mixture was then poured into water and the compound was extracted with dichloromethane. The organic layer was concentrated under reduced pressure to afford the crude product, which was purified by column chromatography.

4. General procedure for synthesis of dendron-rod coil by Huisgen's 1,3-Dipolar Cycloadditions (Click Reactions) (IV).

Dendron-rod (**18** (G1-dendron-rod), **19** (G2-dendron-rod), or **20** (G3-dendron-rod)) (1.2 equiv) and polymeric coil (**12**) (1.0 equiv), *N,N,N',N',N''*-pentamethyl diethylenetriamine (PMDETA) (4.0 equiv), and Cu(I)Br (4.0equiv) were added to a flask and anhydrous THF was used as a solvent. The mixture was stirred for 10 min and degassed by three freeze-thaw cycles. The Schlenk flask was placed in a constant temperature oil bath at 25 °C for 24 h. The crude product was purified by column chromatography. The final product was dried under vacuum overnight and analyzed by SEC in THF and ¹H NMR.

Synthesis of compound 6: (dihydroxy benzthiadiazole)

The above compound was synthesized according to the reported procedure.¹

Synthesis of compound 7:

According to general procedure (II), dihydroxy benzthiadiazole core (**6**) (0.20g, 0.41 mmol), propargyl bromide (0.03 mL, 0.38 mmol), K₂CO₃ (0.15 g, 1.13 mmol) and 18-crown-6 (0.05 g, 0.19 mmol) were reacted in THF solvent. The crude product was purified by column chromatography using ethylacetate:dichloromethane (1:9) as the eluent to afford the product. (0.09g, 43% yield) ¹H NMR (400 MHz, DMSO-D) δ 8.14 (br, 2H), 7.90 (br, 2H), 7.14-7.59 (m, 8H), 6.96 (br, 1H), 6.79 (br, 1H), 4.80 (s, 2H), 2.59 (s, 1H) ¹³C NMR, (400 MHz, DMSO-D) δ 159.0, 158.6, 152, 147.3, 145.5, 138.6, 137.2, 135.9, 135.1, 129.9, 128.3, 125.4, 124.3, 123.4, 118.6, 116.7, 115.3, 113.7, 112.1, 73.2, 70.1, 58.2.

Synthesis of compound 28:

According to general procedure (II), compound (**7**) (0.20g, 0.40 mmol), benzyl bromide (0.05 mL, 0.42 mmol), K₂CO₃ (0.16 g, 1.15 mmol) and 18-crown-6 (0.05 g, 0.19 mmol) were reacted in THF solvent. The crude product was purified by column chromatography using hexanes:ethylacetate (9:1) as the eluent to afford the product. (0.16 g, 70% yield) ¹H NMR (400 MHz, CDCl₃) δ 8.13 (s, 2H), 7.91 (s, 2H), 7.38 (m, 13H), 7.02 – 6.91 (m, 2H), 5.15 (s, 2H), 4.78 (s, 2H), 2.57 (s, 1H). ¹³C NMR (400 MHz, CDCl₃): δ 159.2, 157.9, 145.6, 138.7, 136.8, 135.3, 130.1, 129.0, 127.5, 125.6, 123.9, 119.6, 118.7, 114.4, 112.3, 69.9, 55.9.

Synthesis of compound 29:

A mixture of N-(4-decyl)phenylpyren-1-amine (5.00 g, 11.53 mmol), 2-(3-bromophenyl)-1,3-dioxolane (3.96 g, 17.30 mmol), Pd(dba)₂ (0.05 g, 0.06 mmol), (t-Bu)₃P (0.06 g, 0.11 mmol), and toluene (100mL) was heated at 80 °C for 8 h. After cooling, the mixture was poured into ice water and extracted with diethyl ether (3 × 30 mL) and the combined extract was dried over anhydrous MgSO₄ and evaporated to yield a yellow syrup which was further purified by column chromatography using dichloromethane:hexane (1:1) as the eluent to yield a pale yellow solid as the product (5.50 g, 82% yield). ¹H NMR (400 MHz, ((CD₃)₂CO) δ 7.67-8.46 (m, 9H), 6.90-7.66 (m, 8H), 5.62 (s, 1H), 3.81-4.00 (m, 4H), 2.50-2.62 (m, 2H), 1.60 (br, 2H), 1.29 (br, 14H), 0.85 (br, 3H). ¹³C NMR, (400 MHz, ((CD₃)₂CO) δ 149.4, 146.4, 139.2, 137.4, 129.8, 129.5, 128.1, 128.0, 127.9, 126.6, 126.5, 125.4, 125.3, 125.3, 123.8, 119.3, 104.1, 65.4, 35.7, 32.2, 31.8, 30.0, 29.7, 23.0, 14.5.

Synthesis of compound 30:

A suspension of compound **29** (2.21 g, 3.80 mmol) in glacial acetic acid (25 mL) was heated to 50 °C. After a clear solution is formed, 4 mL of water was added and the temperature was maintained at 50 °C for 3 h. The mixture was cooled and added 50 mL ice water. The mixture was extracted with ethyl acetate and washed several times with water, NaHCO₃ solution and passed over Na₂SO₄. The organic layer was collected and dried under reduced pressure and flushed through the column. A yellow solid was obtained as the product (1.59 g, 78% yield). ¹H NMR (400 MHz, CDCl₃) δ 9.79 (s, 1H), 8.30 – 7.67 (m, 9H), 7.59 – 6.93 (m, 8H), 2.59 – 2.47 (m, 2H), 1.53 (d, *J* = 1.0, 2H), 1.23 (s, 14H), 0.84 (t, *J* = 6.5, 3H). ¹³C NMR (400 MHz, CDCl₃) δ 192.8, 150.2, 145.6, 140.4, 138.5, 137.8, 131.6, 131.3, 130.2,

130.1, 129.8, 128.5, 127.8, 127.7, 127.5, 126.7, 126.6, 126.5, 126.2, 125.7, 125.6, 125.1, 123.8, 123.3, 122.2, 120.9, 35.7, 32.3, 31.8, 29.9, 23.0, 14.5.

Synthesis of compound 16:

According to general procedure (III), compound **30** (1.99 g, 3.70 mmol) was dissolved in 20 mL tetrahydrofuran and diluted with 30 mL methanol. Sodium borohydride (0.17 g 4.44 mmol) was added in portions with efficient stirring. After the addition was complete the mixture was allowed to stir overnight. The mixture was poured into water and the compound was extracted with diethyl ether. The organic extract was collected, dried over anhydrous MgSO_4 and evaporated to yield a yellow solid. This was purified by column chromatography using dichloromethane/hexane (1:1) mixture as the eluent to yield a yellow powder as the product (1.95 g, 98% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.80-8.21 (br, 9H), 7.12 (br, 1H), 6.88-7.07 (br, 7H), 4.52 (s, 2H), 2.53 (br, 2H), 1.39 (br, 2H), 1.25 (br, 14H), 0.87 (br, 3H). ^{13}C NMR, (400 MHz, CDCl_3) δ 148.9, 148.5, 142.3, 141.3, 137.3, 131.5, 131.3, 129.8, 129.6, 129.5, 128.5, 128.1, 127.9, 127.5, 127.3, 126.6, 126.5, 126.3, 125.4, 125.3, 125.1, 123.7, 123.1, 120.7, 119.9, 119.8, 65.5, 35.6, 32.2, 31.8, 29.8, 23.0, 14.5.

Synthesis of compound 31:

According to general procedure (I), compound **16** (10.0 g, 18.53 mmol), triethylamine (6.5 mL, 37.05 mmol), mesyl chloride (2.87 mL, 37.05 mmol) and DMAP (catalytic amount) were reacted. After the completion of the reaction, the mixture was worked up and extracted with CH₂Cl₂. The dry crude product was further reacted with LiBr (7.96 g, 92.46 mmol) at reflux. The crude reaction mixture was purified by column chromatography using dichloromethane:hexanes (1:1) to afford the product. (11.20 g 97%) ¹H NMR (400 MHz, CDCl₃) δ 7.79-8.21 (m, 9H), 6.85-7.17 (m, 8H), 4.31 (s, 2H), 2.60 – 2.48 (br, 2H), 1.54 (br, 2H), 1.28 (br, 14H), 0.87 (t, *J* = 6.8, 3H). ¹³C-NMR (400 MHz, CDCl₃) δ 148.9, 148.0, 141.0, 139.0, 131.5, 131.4, 129.9, 129.8, 129.5, 128.5, 128.3, 127.9, 127.5, 127.4, 126.6, 125.5, 125.4, 125.1, 123.6, 123.4, 121.9, 121.2, 121.0, 35.6, 34.1, 32.2, 31.8, 29.9, 23.0, 14.5.

Synthesis of compound **32**:

According to general procedure (II), 3,5 dihydroxybenzyl alcohol (0.93 g, 6.32 mmol), compound **31** (8.0 g, 13.27 mmol), K₂CO₃ (2.70 g, 18.96 mmol) and 18-crown-6 (0.17 g, 0.63 mmol) were refluxed in THF. The crude product was purified by column chromatography using ethylacetate: dichloromethane (1:9) as eluent to yield yellow solid (4.55 g, 56% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.76-8.18 (m, 18H), 7.11-7.21 (m, 2H), 6.86-7.08 (m, 14H), 6.30 (s, 2H), 6.23 (s, 1H), 4.77 (s, 4H), 4.38 (s, 2H), 2.52 (br, 4H), 1.46 (br, 4H) 1.24 (br, 28H), 0.86 (br, 6H). ¹³C NMR, (400 MHz, CDCl₃) δ 160.0, 149.5, 146.3, 143.4, 141.2, 138.2, 127.4, 131.5, 131.3, 129.7, 129.6, 129.5, 128.4, 128.1, 127.9, 127.5, 127.3, 126.6, 126.4, 126.3, 125.4, 124.3, 125.1, 123.7, 123.2, 120.7, 120.4, 120.2, 105.7, 101.2, 70.1, 65.3, 35.6, 32.2, 31.8, 29.9, 23.1, 14.5. MS (MALDI⁺) calcd for C₈₅H₈₆N₂O₃ 1183.60; observed 1182.80.

Synthesis of compound 13:

According to general procedure (I), G1-OH (compound **32**) (3.60 g, 3.04 mmol) was reacted with triethylamine (1.0 mL, 7.60 mmol), DMAP (7.0 mg, 0.06 mmol), mesyl chloride (0.5 mL, 6.08 mmol) and LiBr (1.31 g, 15.20 mmol) to convert it to its corresponding bromide. The crude product was purified by column chromatography using hexane:dichloromethane (1:1) as eluent to afford the product. (3.69g, quantitative yield) ¹H NMR (400 MHz, CDCl₃) δ 7.76-8.20 (m, 18H), 7.10-7.23 (br, 2H), 6.88-7.07 (m, 14H), 6.33 (s, 2H), 6.23 (s, 1H), 4.75 (s, 4H), 4.16 (s, 2H), 2.51 (br, 4H), 1.54 (br, 4H), 1.24 (br, 28H), 0.86 (m, 6H). ¹³C NMR, (400 MHz, CDCl₃) δ 160.0, 149.5, 146.2, 141.2, 139.6, 138.0, 137.5, 131.5, 131.3, 129.8, 129.5, 128.4, 128.2, 127.9, 127.5, 127.3, 126.6, 126.5, 126.3, 125.4, 125.3, 125.1, 123.7, 123.3, 120.7, 120.3, 120.2, 108.2, 102.2, 70.2, 35.7, 33.8, 32.2, 21.8, 29.9, 23.0, 14.5. MS (MALDI⁺) calcd for C₈₅H₈₅N₂O₂Br 1246.50; observed 1200.40.

Synthesis of compound 33:

According to general procedure (II), G1-Br (compound **13**) (3.70 g, 1.52 mmol), 3,5-dihydroxy benzyl alcohol (0.11 g, 0.73 mmol), K₂CO₃ (0.31 g, 2.14 mmol) and 18-crown-6 (0.04 g, 0.07 mmol) were reacted in THF solvent. The crude product was purified by column chromatography using hexane:dichloromethane (1:1) as eluent to afford the product. (1.47 g, 78% yield) ¹H NMR (400 MHz, CDCl₃) δ 7.72-8.15 (m, 36H), 7.08-7.19 (m, 4H), 6.85-7.05 (m, 28H), 6.48 (s, 2H), 6.38 (s, 5H), 6.25 (s, 2H), 4.74 (s, 8H), 4.69 (s, 4H), 4.53 (s, 2H), 2.49 (br, 8H), 1.54 (br, 8H), 1.22 (br, 56H), 0.85 (m, 12H). ¹³C NMR, (400 MHz, CDCl₃) δ 160.3, 149.5, 146.3, 143.6, 141.2, 139.2, 138.2, 137.4, 131.5, 131.4, 129.8, 129.7, 129.5, 128.4, 128.2, 127.9, 127.5, 127.3, 126.6, 126.5, 126.3, 125.4, 125.3, 125.1, 123.7, 123.2, 120.7, 120.3, 106.6, 105.9, 101.6, 70.2, 65.6, 35.7, 32.2, 31.8, 29.9, 23.0, 14.5. MS (MALDI+) calcd for C₁₇₇H₁₇₆N₄O₇ 2471.31; observed 2470.00.

Synthesis of compound **14**:

According to general procedure (I), G2-OH compound **33** (1.00 g, 0.41 mmol) was reacted with triethylamine (0.14 mL, 1.02 mmol), DMAP (1.00 mg, 0.08 mmol), mesyl chloride (0.06 mL, 0.81 mmol) and LiBr (0.17 g, 2.03 mmol) to convert it to its corresponding bromide. The crude product was isolated by column chromatography using hexanes:dichloromethane (1:1) to afford the product (1.03 g, quantitative yield) ¹H NMR (300 MHz, CDCl₃) δ 7.71-8.15 (m, 36H), 7.07-7.31 (m, 4H), 6.85-7.04 (m, 28H), 6.49 (s, 2H), 6.35 (s, 5H), 6.25 (s, 2H), 4.74 (s, 8H), 4.64 (s, 4H), 4.33 (s, 2H), 2.49 (br, 8H),

1.54 (br, 8H), 1.22 (br, 56H), 0.85 (m, 12H). ^{13}C NMR, (300 MHz, CDCl_3) δ 159.8, 149.11, 145.9, 140.8, 139.5, 138.5, 137.7, 137.0, 131.1, 130.9, 129.4, 129.3, 128.0, 127.7, 127.5, 127.1, 126.9, 126.2, 126.0, 125.9, 125.0, 124.9, 124.7, 123.3, 122.8, 120.3, 120.0, 119.8, 107.9, 106.2, 101.3, 69.7, 35.2, 33.5, 31.8, 29.5, 22.6, 14.1. MS (MALDI⁺) calcd for $\text{C}_{117}\text{H}_{175}\text{BrN}_4\text{O}_6$ 2534.21; observed 2534.50.

Synthesis of compound 34:

According to general procedure (II), G2Br (compound **14**) (1.43 g, 0.56 mmol), 3,5-dihydroxy benzyl alcohol (0.03 g, 0.27 mmol), K_2CO_3 (0.12 g, 0.86 mmol) and 18-crown-6 (0.07 g, 0.03 mmol) were reacted in THF solvent. The crude product was purified by column chromatography using hexanes:dichloromethane (1:1) to afford the product. (0.63 g, 53% yield) ^1H NMR (400 MHz, CDCl_3) δ 7.62-8.22 (m, 72H), 6.78-7.20 (m, 63H), 6.49 (s, 8H), 6.32 (s, 10H), 6.26 – 6.16 (m, 4H), 4.87 (s, 4H), 4.57-4.76 (s, 24H), 4.47 (s, 2H), 2.46 (br, 16H), 1.55 (br, 16H), 1.20 (br, 112H), 0.84 (br, 24H). ^{13}C NMR (400 MHz, CDCl_3) δ 160.4, 149.3, 145.9, 140.4, 138.2, 136.3, 130.9, 128.7, 127.5, 126.0,

124.8, 123.3, 120.3, 106.5, 106.1, 70.2, 35.0, 31.6, 29.3, 22.1, 14.0. MS (MALDI+) calcd for $C_{361}H_{356}N_8O_{15}$ 5046.73; observed 5048.20.

Synthesis of compound 15:

According to general procedure (I), compound **34** (0.50 g, 0.09 mmol) was reacted with triethylamine (0.04 mL, 0.25 mmol), DMAP (0.002 g, 0.002 mmol), mesyl chloride (0.02 mL, 0.19 mmol) and LiBr (0.04 g, 0.50 mmol) to convert to its corresponding bromide. The crude product was purified by column chromatography using dichloromethane to afford the product. (0.21 g, 40 %yield) 1H NMR (400 MHz, $CDCl_3$) δ 7.65-8.22 (m, 72H), 6.79-7.15 (m, 63H), 6.51 (s, 8H), 6.32 (s, 10H), 6.21 (s, 4H), 4.81 (s, 4H), 4.53-4.74 (s, 24H), 4.25 (s, 2H), 2.46 (br, 16H), 1.54 (br, 16H), 1.20 (br, 112H), 0.84 (br, 24H). ^{13}C NMR, (400 MHz, $CDCl_3$) δ 159.6, 149.0, 145.9, 140.7, 139.0, 137.9, 136.5, 131.0, 129.3, 128.2, 127.9, 126.2, 124.8, 123.4, 122.7, 120.3, 119.6, 106.2, 69.7, 34.9, 31.8, 29.7, 22.5, 14.2. MS (MALDI+) calcd for $C_{361}H_{355}BrN_8O_{14}$ 5109.63; observed 5107.7.

Synthesis of compound 18:

According to general procedure (II), compound **7** (0.04 g, 0.08 mmol), G1-Br (compound **13**) (0.10 g, 0.08 mmol), K₂CO₃ (0.03 g, 2.20 mmol) and 18-crown-6 (2.00 mg, 0.008 mmol) were reacted in THF solvent. The crude product was purified by column chromatography using hexanes:ethyl acetate (7:3) to afford the product. (0.05 g, 48% yield) ¹H NMR (400 MHz, CDCl₃) δ 7.74-8.20 (m, 22H), 7.11-7.46 (m, 12H), 6.88-7.08 (br, 13H), 6.82 (d, *J* = 6.4, 1H), 6.47 (s, 2H), 6.30 (s, 1H), 4.71-4.92 (m, 8H), 2.57 (s, 1H), 2.51 (br, 4H), 1.56 (br, 4H), 1.26 (br, 28H), 0.87 (t, *J* = 6.8, 6H). ¹³C NMR, (400 MHz, CDCl₃) δ 159.8, 159.0, 158.0, 152.4, 149.2, 145.9, 145.3, 145.1, 140.8, 138.9, 138.6, 137.8, 137.1, 135.5, 135.3, 131.1, 129.9, 129.4, 129.1, 128.5, 128.1, 127.8, 127.6, 127.2, 126.9, 126.3, 125.9, 125.7, 125.3, 124.7, 124.4, 123.3, 122.8, 120.5, 119.9, 119.2, 118.6, 113.9, 112.5, 106.2, 101.5, 69.7, 55.6, 35.2, 31.8, 29.4, 22.1, 13.8 MS (MALDI⁺) calcd for C₁₁₄H₁₀₂N₄O₄S₃ 1688.25; observed 1687.00.

Synthesis of compound 19:

According to general procedure (II), compound **7** (0.02 g, 0.04 mmol), G2-Br (compound **14**) (0.10 g, 0.04 mmol), K₂CO₃ (0.02 g, 0.11 mmol) and 18-crown-6 (1.00 mg, 0.004 mmol) were reacted in THF solvent. The crude product was purified by column chromatography using hexanes:ethyl acetate (7:3) to afford the product. (0.17g, 75% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.52-8.31 (m, 40H), 7.27-7.47 (m, 10H), 7.06-7.21 (m, 4H), 6.79-7.08 (m, 28H), 6.62 (s, 2H), 6.37 (s, 5H), 6.25 (s, 2H), 4.92-5.07 (s, 4H), 4.63-4.84 (s, 12H), 2.57 (br, 1H), 2.47 (br, 8H), 1.56 (br, 8H), 1.11-1.39 (br, 56H), 0.84 (m, 12H). ¹³C NMR, (400MHz, CDCl₃) δ 160.1, 159.7, 159.1, 157.9, 152.4, 149.1, 145.9, 145.3, 145.0, 140.9, 139.2, 138.8, 137.9, 137.0, 135.6, 131.2, 131.0, 129.9, 129.5, 129.3, 129.1, 128.6, 128.1, 127.9, 127.5, 127.3, 127.1, 126.3, 126.0, 125.7, 125.3, 125.1, 124.8, 124.3, 123.4, 122.9, 120.4, 120.1, 119.7, 119.2, 118.5, 114.1 112.5, 106.2, 101.2, 70.1, 55.9, 35.2, 31.4, 29.4, 22.5, 13.8. MS (MALDI+) cald for C₂₀₆H₁₉₂N₆O₈S₃ 2975.96; observed 2975.8.

Synthesis of compound **20**:

According to general procedure (II), compound **7** (0.01 g, 0.03 mmol), G3-Br (compound **15**) (0.15 g, 0.03 mmol), K₂CO₃ (0.01 g, 0.08 mmol) and 18-crown-6 (3.00 mg, 0.01 mmol) were reacted in THF solvent. The crude product was purified by column chromatography using hexanes:dichloromethane (1:1) to afford the product. (0.03 g, 19% yield) ¹H NMR (400 MHz, CDCl₃) δ 7.67-8.11 (m, 76H), 6.80-7.14 (m, 72H), 6.63 (s, 1H), 6.51 (br, 8H), 6.30 (br, 10H), 6.19 (br, 4H), 4.81-4.98 (br, 8H), 4.53-4.71 (m, 24H), 2.54 (s, 1H), 2.44 (br, 16H), 1.55 (br, 16H), 1.20 (br, 112H), 0.83 (br, 24H). ¹³C NMR, (400 MHz, CDCl₃) δ 160.0, 149.3, 145.9, 141.0, 137.9, 136.9, 131.4, 129.3, 128.2, 127.2, 125.8, 125.1, 122.7, 119.6, 35.2, 31.4, 29.1, 22.5, 13.8. MS (MALDI+) calcd for C₃₈₈H₃₇₆N₁₀O₁₆S₃ 5531.39; observed 5548.30.

Synthesis of compound **9**:

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Naphthaene dianhydride (15.0 g, 0.55 mol) was taken into a three-necked flask with freshly distilled DMF. The slurry was heated to about 140 °C under N₂ atmosphere. To this, decylamine (11.1 mL, 0.55 mol) was added dropwise for about 10 minutes and the reaction mixture was refluxed overnight. After the complete consumption of naphthalene dianhydride, 3-amino-1-propanol (4.2 mL, 0.55 mol) was added and the mixture was left at reflux for overnight. After the completion of the reaction, the mixture was cooled down and DMF was evaporated under low pressure. The residue was partitioned using dicholoromethane/water, dried over MgSO₄. The organic layer was collected and concentrated under low pressure. The crude product was purified by column chromatography using 30% dicholomethane in hexanes. ¹H NMR (400 MHz, CDCl₃) δ 8.72 (s, 4H), 4.45(br, 2H), 4.20 (br, 2H),

3.68 (br, 2H), 1.98 (br, 2H), 1.75(2H), 1.30 (br, 14H), 0.98 (br, 3H) ^{13}C -NMR (400 MHz, CDCl_3) δ 163.5, 131.2, 120.6, 59.2, 40.4, 36.4, 31.8, 29.5, 29.3, 28.1, 27.1, 22.7, 14.1.

Synthesis of monomer 10:

10

Compound **9** (1.32 g, 2.84 mmol) and a catalytic amount of DMAP was placed into a round bottom flask and THF was added as a solvent. The solution was cooled to 0°C and triethylamine (0.79 mL, 5.67 mmol) was added followed by methacryloyl chloride (0.55 mL, 5.67 mmol). The mixture was left at room temperature overnight. After the completion of the reaction, the mixture was extracted using water and dichloromethane. Organic layer was collected and evaporated under reduced pressure. The crude product was purified by column chromatography using dichloromethane to afford pale yellow solid as a product (0.79g, 49% yield). ^1H NMR (400 MHz, CDCl_3) δ 8.78 (s, 4H), 6.12 (m, 1H), 5.54 (m, 1H), 4.30 (m, 6H), 2.20 (m, 2H), 1.76 (m, 2H), 1.45 (s, 3H), 1.28 (m, 14H), 0.89 (s, 3H). ^{13}C -NMR (400 MHz, CDCl_3) δ 167.2, 163.1, 136.3, 131.3, 131.1, 126.8, 126.3, 125.4, 63.7, 41.0, 38.2, 31.9, 29.5, 29.1, 28.0, 27.4, 26.9, 22.5, 18.3, 14.1.

Synthesis of compound 35:

35

To the round bottom flask, 0.25 g (3.08 mmol) chloroethanol and 0.30g (4.61 mmol) sodium azide were taken and 5 mL DMSO was added as a solvent. The mixture was heated at 100°C for overnight. After the completion of the reaction, water was added and the mixture was extracted with dichloromethane (3x25 mL). The organic layer was combined and the solvent was evaporated. The

product was obtained without any purification. ^1H NMR (400 MHz, CDCl_3) δ 5.24 (s, 1H), 3.68 (m, 2H), 3.31 (m, 2H) ^{13}C -NMR (400 MHz, CDCl_3) δ 60.7, 53.3.

Synthesis of Initiator 11:

11

0.25 g (0.99 mmol) of 2-azidoethanol (compound **35**) and 0.96 g (1.99 mmol) 2-bromoisobutyric acid were dissolved in 30 mL dichloromethane. The reaction mixture was cooled down in ice-water bath and a solution of 1.18 g (1.99 mmol) dicyclohexyl carbodiimide in 10 mL dichloromethane was slowly added while stirring. A solution of 0.17 g (0.49 mmol) 4-dimethylaminopyridine in 5 mL dichloromethane was subsequently added. The mixture was stirred at 0°C for 1 hour and then at room temperature for 24 hours. The precipitated dicyclohexyl urea was filtered on cotton twice and washed with dichloromethane. The solution was extracted with a solution of NaHCO_3 (5%) followed by dichloromethane (3x25 mL) and dried over MgSO_4 . The volatiles were removed under reduced pressure and the crude product was purified by column chromatography using 10% ethyl acetate in hexane. The product was obtained as a colorless liquid with a quantitative yield. ^1H NMR (400 MHz, CDCl_3) δ 4.34 (br, 2H), 3.53 (br, 2H), 1.96 (s, 6H) ^{13}C -NMR (400 MHz, CDCl_3) δ 171.4, 64.6, 55.2, 49.6, 30.6.

Synthesis of Polymeric coil (12):

12

4mg (0.03 mmol) of Cu(I)Br was taken in a 5 mL round bottom flask equipped with a septum and gas inlet/outlet. The flask was degassed with argon for 5 min. Then, 12μL (0.06 mmol) of *N,N,N',N',N''*-pentamethyl diethylenetriamine (PMDETA) was added and stirred for 5 more minutes. To this reaction mixture, the solution of the monomer **35** (800 mg, 1.5 mmol) in 400 μL degassed anisole was added and it was stirred for another 5 minutes. To this mixture, 5 μL (0.03 mmol) of the initiator **11** was added and the flask was transferred to a preheated oil bath at 65 °C. The polymerization was carried out at the same temperature under argon atmosphere for 6 h. After that, the reaction was stopped and the polymer was dissolved in THF. The polymer solution was filtered through silica to remove copper salt and then precipitated from diethylether and dried over vacuum for 6 h. The polymer was obtained as a yellow-brown solid with 58% yield. $M_n = 9326$; PDI = 1.14; Degree of polymerization = 17.

Synthesis of **1** (G1 dendron-rod-coil):

According to general procedure (IV), compound **18** (19 mg, 11 μmole), polymer **12** (75 mg, 9.2 μmole), CuBr (5.3 mg, 37 μmole) and PMDETA (8 μL, 37 μmole) were used. After the completion of the reaction, the THF in the mixture was removed by evaporation and the dry crude product was

Synthesis of **3** (G3 dendron-rod-coil):

According to general procedure (IV), compound **20** (76 mg, 11 μ mole), polymer **12** (75 mg, 9.2 μ mole), CuBr (5.3 mg, 37 μ mole) and PMDETA (8 μ L, 37 μ mole) were used. After the completion of the reaction, the THF in the mixture was removed by evaporation and the dry crude product was purified by column chromatography using dichloromethane:THF (0-5%) to afford the product. (62mg, 41%), SEC, M_n = 13200, PDI = 1.09.

Synthesis of **21** (rod-coil):

According to general procedure (IV), compound **28** (7 mg, 11 μ mole), polymer **12** (75 mg, 9.2 μ mole), CuBr (5.3 mg, 37 μ mole) and PMDETA (8 μ L, 37 μ mole) were used. After the completion of the reaction, the THF in the mixture as removed by evaporation and the dry crude product was purified by column chromatography using dichloromethane:THF (0-5%) to afford the product. (34mg, 40%), SEC, $M_n = 9980$ PDI = 1.08.

Synthesis of compound **36**:

1.00 g (4.78 mmol) of 8-bromooctanoic acid was placed in a round bottom flask and 20 mL of dichloromethane was added as a solvent. To this solution, 0.83 mL (9.57 mmol) of oxalyl chloride was slowly added. The reaction mixture was stirred at room temperature for 6 hrs. Then, the solvent was removed by rotary evaporator to yield the corresponding acid chloride which was further used for the next step without purification.

To the round bottom flask, 1.09 g (4.78 mmol) of acid chloride, 1.11 g (2.38 mmol) of compound **9**, 0.45 mL (4.78 mmol) of triethylamine, and catalytic amount of DMAP were added and THF was used as a solvent. The mixture was stirred at room temperature for overnight. After the completion of the reaction, water was added and the mixture was partitioned using dichloromethane and water. The organic layer was collected and concentrated using a rotary evaporator. The product was purified by column chromatography using 50:50 Hexanes:Dichloromethane to afford the product (0.37 g, 23 %yield) ^1H NMR (400 MHz, CDCl_3) δ 8.79 (s, 4H), 4.35 (t, $J = 7.1$, 2H), 4.27 – 4.15 (m, 4H), 3.43 (m, 4H), 1.94 – 1.86 (m, 4H), 1.66 (m, 4H), 1.36 (m, 20H), 0.89 (t, $J = 6.7$, 3H). ^{13}C -NMR (400 MHz, CDCl_3) δ 173.0, 162.3, 130.9, 126.4, 61.8, 45.1, 41.0, 38.1, 34.2, 32.6, 31.9, 29.6, 29.3, 28.9, 28.5, 28.1, 27.4, 27.0, 26.6, 24.8, 22.5, 14.2.

Chemical structure of compound **27**, a complex organic molecule. The structure features a central benzothiazine core (a benzene ring fused to a six-membered ring containing one nitrogen and one sulfur atom). This core is substituted with several functional groups: a long alkyl chain ($C_{10}H_{21}$), a triazole ring, and a phthalimide group. The molecule is labeled **27** in the center.

According to general procedure (IV), compound **18** (19 mg, 11 μ mole), the azide functionalized naphthalene bisimide derivative (8 mg, 9.2 μ mole), CuBr (5.3 mg, 37 μ mole) and PMDETA (8 μ L, 37 μ mole) were used. After the completion of the reaction, the THF in the mixture as removed by evaporation and the dry crude product was purified by column chromatography using dichloromethane:THF (0-5%) to afford the product. (22mg, 78%), ^1H NMR (400 MHz, CDCl_3) δ 8.62 (s, 4H, a), 8.16 – 7.55 (m, 22H, b, c, d), 7.39 – 6.87 (m, 26H, e), 6.88 – 6.74 (m, 1H, f), 6.46 (s, 2H, g), 6.30 (s, 1H, h), 5.29 (s, 2H, i), 4.81 (s, 6H, j), 4.01-4.38 (m, 8H, k), 2.57 – 2.43 (m, 4H, l), 2.26 (m, 2H, m), 2.07 (m, 2H, n), 1.93 (m, 2H, o), 1.59 (m, 28H, p, q, r), 1.24 (br, 28H, s), 0.85 (br, 9H, t) ^{13}C

NMR (400 MHz, CDCl₃) δ 174.2, 162.7, 159.7, 158.5, 152.4, 149.3, 145.5, 143.5, 140.9, 138.8, 137.9, 137.1, 135.4, 131.3, 131.0, 130.0, 129.2, 128.6, 127.9, 127.8, 127.4, 127.2, 126.9, 126.6, 126.3, 126.1, 126.9, 125.6, 125.3, 125.0, 124.8, 124.2, 123.4, 122.9, 122.6, 120.4, 120.1, 119.9, 118.9, 111.9, 106.9, 101.5, 69.4, 62.5, 50.7, 35.3, 34.0, 31.9, 31.4, 29.7, 28.8, 27.5, 27.0, 26.1, 24.7, 22.7, 14.1 SEC, M_n = 2700, PDI = 1.03.

Figure S1. The SEC profile of formation Dendron-rod-coil *via* click chemistry

Reference:

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