

Supporting information.

A Synthetic Approach to Fullerene-rich Dendron and Its Linear Polymer via Ring-Opening Metathesis Polymerization.

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Experimental Section

Materials and Instruments: All starting materials were purchased either from Aldrich or Acros and used without further purification. All solvents are ACS grade unless otherwise noted. Anhydrous THF was obtained by distillation from sodium/benzophenone prior to use. Anhydrous toluene was used as received from Aldrich. Dendritic alcohol¹ and PCBA² were prepared according to established literature procedures. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury Vx 200 MHz or a VNMRS 600 (Varian, USA) spectrophotometer using CDCl₃ as solvent and referenced to the solvent peak. Number-average (M_n) and weight average (M_w) molecular weights, and polydispersity index (PDI) of the polymer products were determined by gel permeation chromatography (GPC) with Agilent 1200 HPLC Chemstation using a series of mono disperse polystyrene as standards in

chlorobenzene (HPLC grade) at 308 K.

Photovoltaic cells fabrication and testing: Bulk heterojunction (BHJ) solar cell devices were fabricated according to the following procedure. First, the ITO coated glass substrate was cleaned with detergent, then ultrasonicated in distilled water, acetone and isopropyl alcohol, and then dried overnight in an oven at 100 °C. Poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT:PSS) (Baytron PH), was spin-cast at 4000 rpm for 40 s. The substrate was then dried for 10 min at 140 °C in air. Subsequently, it is moved into a glove box for spincoating the active layer. A mixed solution of P3HT:dendritic fullerene in *o*-dichlorobenzene (*o*-DCB) was then spin coated at 1000 rpm for 60 s on top of the PEDOT:PSS layer to obtain a BHJ film. Those samples were brought into a vacuum system (about 10^{-7} Torr), and an Al electrode (100 nm) was deposited on top of the BHJ layer. The samples were not exposed to ambient air after being loaded into the glove box. Post annealing was carried out at 150 °C for 5min inside a nitrogen filled glovebox. Measurements were carried out with the solar cells inside the glove box by using a high quality optical fiber to guide the light from the solar simulator equipped with a Keithley 2635A source measurement unit. The solar cell devices were illuminated at an intensity of 100 mW/cm².

Synthesis of fullerene-rich dendron

A flask equipped with a reflux condenser and a drying tube was charged with 4-(2-ethylhexyloxy)-[6,6]-phenyl C₆₁-butyric acid methyl ester (PCBA) (0.75 g, 0.73 mmol) and benzene (50 mL). To this mixture was added oxalyl chloride (0.11 g, 0.876 mmol) and one drop of *N,N*-dimethylformamide (catalyst). The reaction mixture was heated at 80 °C overnight (bubbling observed), then the reaction was cooled and the solvent was removed *in vacuo*. The crude solid was dissolved in anhydrous toluene (20 mL) and filtered. The solvent was removed *in vacuo* to give the benzoyl chloride compound and used without further purification. To the benzoyl chloride in 15 mL of *o*-DCB, dendritic alcohol (50 mg, 0.10

mmol) and DMAP (32mg) in triethylamine (3 mL) and pyridine (3 mL) was added. The mixture was degassed by gently bubbling argon for 30 min and stirred at 40 °C overnight. The solvent was removed *in vacuo*. The crude product was purified by chromatography on silica with 0-10 % ethylacetate in toluene as eluent. Isolated yield = 170 mg (38 %) as a brown solid. GPC: $M_n = 1.81$ kDa, $M_w = 1.86$ kDa, PDI = 1.03; ^1H NMR (200 MHz, CDCl_3): δ ppm 7.81 (8H, d, J = 8.71 Hz), 7.03 (8H, d, J = 8.71 Hz), 6.24 (2H, s), 4.72 (2H, m), 4.39 (2H, m), 4.17 (8H, m), 3.90 (8H, m), 3.21 (2H, m), 2.89 (8H, m), 2.62-2.41 (10H, m), 2.23-2.04 (8H, m), 1.79 (4H, m), 1.65-1.10 (43H, m), 1.00-0.89 (24H, m).

Synthesis of fullerene-rich linear polymer

A volumetric flask was charged with 4 mg of third generation ruthenium Grubbs catalyst. The flask was capped with a septum, evacuated under high vacuum and back filled with argon. This was repeated two more times. The catalyst was then dissolved in a small amount of THF and the resulting solution was made up to 1 mL, to yield a standard solution having a concentration of 4.52×10^{-3} M.

Exo norbornene fullerene-rich dendron (70.0 mg, 15.5 μmol) was placed in a 5 mL vial with a magnetic stir bar and a septum cap. The vial was evacuated and back-filled with argon three times. Anhydrous *o*-DCB (0.3 mL) was then introduced via syringe and 34 μL of the ruthenium catalyst solution was rapidly injected. After stirring the contents for every 1.5 hs, additional 34 μL of the ruthenium catalyst solution was gradually injected. The reaction completion was monitored by TLC and after 12 hours, quenched by the addition of ethyl vinyl ether (*ca.* 30 μL) and the mixture stirred for a further 3 h. The mixture was then diluted with chlorobenzene to ensure complete solubility (1.5 mL), and the solution was added dropwise to MeOH (15 mL), centrifuged and decanted. The precipitate was treated with MeOH several times in the same manner. The product was washed with diethylether and dried *in vacuo* to afford 67 mg (95 %). GPC: $M_n = 6.50$ kDa, $M_w = 7.02$ kDa, PDI = 1.08; ^1H

NMR (200 MHz, CDCl₃): δ ppm 7.76 (8H, brs.), 7.01 (8H, brs), 5.63 (2H, brs), 4.69-4.34 (6H, brs), 4.17 (8H, brs), 3.88 (8H, brs), 2.81 (8H, brs), 2.47 (10H, brs), 2.21 (8H, brs), 1.75 (4H, brs), 1.60-1.11 (43H, brs), 1.03-0.81 (24H, brs).

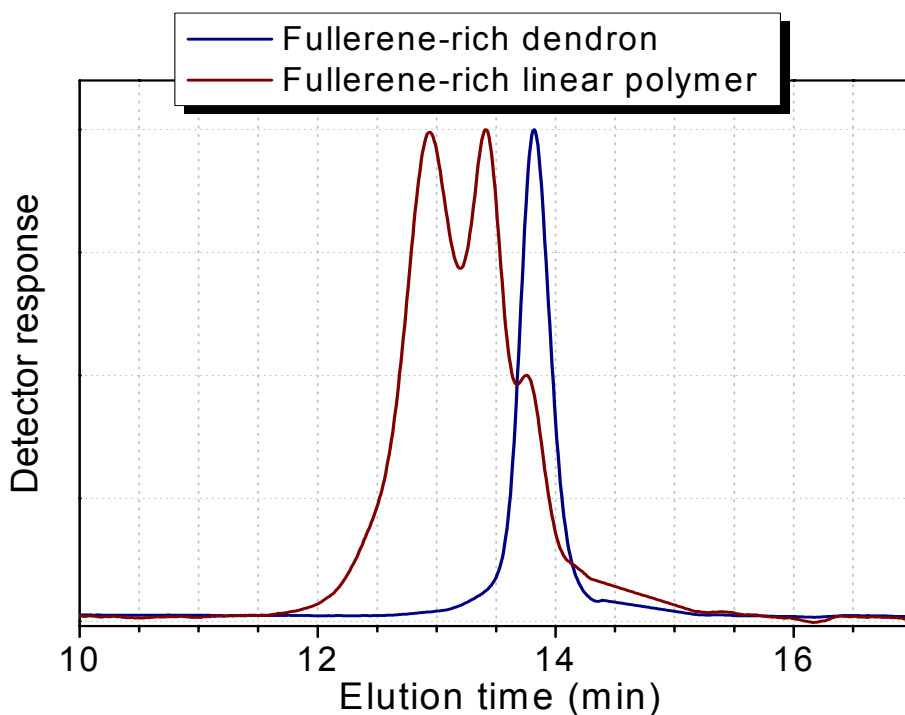


Figure S1. Gel permeation chromatography analysis of fullerene-rich dendron ($M_n = 1,810$ Da, PDI = 1.03) and fullerene-rich linear polymer (monomer/catalyst = 100, $M_n = 4,205$ Da, PDI = 1.43). Solvent, chlorobenzene; flow rate, 1.0 mL/min; detector, refractive index.

1. S. Rajaram, T.-L. Choi, M. Rolandi and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 2007, **129**, 9619-9621.
2. C. Yang, J. Y. Kim, S. Cho, J. K. Lee, A. J. Heeger and F. Wudl, *J. Am. Chem. Soc.*, 2008, **130**, 6444-6450.