Synthesis and Characterisation of Monodisperse Branched Fullereneterminated Poly(ethylene glycol)s

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Figure S1 Transesterification reaction of PEG_{~15}(OH)₄ and PCBM monitored by ¹H NMR: Integration of acyloxymethylene protons (normalised to main PEG backbone at 3.66 ppm) versus time (2, 24, 48, 72, 96 and 120 hr)



Figure S2 Full positive ionization MALDI-TOF spectrum of PCBM (MW = 910.88 g mol⁻¹) using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. Matrix peak denoted by (*).



Figure S3 ¹H NMR spectrum of PEG_{~4}(OCOCF₃)₂, prepared *in situ* from 1.



Figure S4 ¹H NMR spectrum of PEG_{~21}(OCOCF₃)₃, prepared *in situ* from 2.



Figure S5 ¹H NMR spectrum of PEG_{~15}(OCOCF₃)₄, prepared *in situ* from **3**. The singlet at 4.42 ppm, is thought to correspond to acylation of the CH₂OH stub linked to the central quaternary carbon atom.



Figure S6 ¹³C NMR spectrum of PEG_{~21}(OCOCF₃)₄, prepared *in situ* from **3**. (*) denoted two possible quaternary carbon centres.



Figure S7 ¹³C DEPT 135° NMR spectrum of PEG_{~21}(OCOCF₃)₄, prepared *in situ* from **3**.

The ¹H NMR spectrum was recorded for $PEG_{\sim 15}(OCOCF_3)_4$ (*Figure S5*). Adjacent to the main acyloxy methylene triplet (**a**, 4.52 ppm) can be seen a small singlet (4.42 ppm) which

exhibits no coupling to neighbouring protons (unlike signal **a**). This signal is consistent with acylation of the stub arm, $F_3CCO_2CH_2C(CH^a_2OPEGOCOCF_3)_3$. The ratio of the integrals of these peaks (*ca.* 7:1), suggests that around half of **3** has a stub arm. The ¹³C NMR spectrum was recorded for $PEG_{-15}(OCOCF_3)_4$ (*Figure S6*). Two signals, not one, of approximately the same intensity, at 45.8 and 46.7 ppm, were observed in the range of the single quaternary carbon expected at the centre of the starting $PEG_{-15}(OH)_4$ (**3**). The two peaks are consistent with approximately half of the star having a short arm. In the ¹³C DEPT 135° (distortion enhancement by polarisation transfer) NMR spectrum of $PEG_{-15}(OCOCF_3)_4$ (*Figure S7*) the two signals at 45.8 and 46.7 ppm are absent, demonstrating that they are both quaternary centres.



Figure S8 Full positive ionization MALDI-TOF spectrum of $PEG_{\sim 21}(OH)_3$ (2) using DCTB as matrix. The polymer peaks are observed at 863 – 1303 m/z and no matrix peaks are observed. All other peaks are attributed to noise.



Figure S9 Full positive ionization MALDI-TOF spectrum of PEG_{~15}(OH)₄ (3) using DCTB as matrix. The polymer peaks are observed at 643 - 1094 m/z. Matrix peaks are denoted as (*) and all other peaks are attributed to noise.



Figure S10 Full positive ionization MALDI-TOF spectrum of $PEG_{4}(OPCB)_{2}$ (4) using DCTB as matrix. The polymer peaks are observed at around 2000 m/z (enlarged peak distribution is shown in

manuscript Figure 1A) and matrix peaks are denoted as (*).



Figure S11 ¹H NMR spectrum of PEG_{~4}(OPCB)₂(4). Vacuum grease signals at 1.28 and 0.9 ppm.



Figure S12 ¹H NMR spectrum of PEG_{~21}(OPCB)₃ (**5a**) and PEG_{~21}(OPCB)₂(OH) (**5b**). Vacuum grease signals at 1.27 and 0.93 ppm.



Figure S13 Full positive ionization MALDI-TOF spectrum of PEG_{~21}(OPCB)₃ (**5a**) and PEG_{~21}(OPCB)₂(OH) (**5b**). Polymer distributions are observed at around 1741, 2752, and 3630 m/z respectively. Short chain fragmentation peaks are observed at lower mass region (< 800 m/z). Matrix peaks are denoted as (*).



Figure S14 Comparison of the number of repeating units on each fragment in MALDI-TOF spectrum of PEG₋₂₁(OPCB)₃ (**5a**) and PEG₋₂₁(OPCB)₂(OH) (**5b**) with Na⁺ ion. Annotation indicate the observed molecular mass of the signals. The red dotted line denotes 20 repeating units.



Figure S15 ¹H NMR spectrum of PEG_{~15}(OPCB)₄ (**6a**) and PEG_{~15}(OPCB)₃(OH) (**6b**). Signals at 1.67 ppm indicate the presence of residual water, and vacuum grease signals are observed at 1.29 and 0.92 ppm.



Figure S16 Full positive ionization MALDI-TOF spectrum of $PEG_{\sim 15}(OPCB)_4$ (6a) and $PEG_{\sim 15}(OPCB)_3(OH)$ (6b). Polymer distributions are observed at around 2200, 3400, and 4300 m/z respectively. Short chain fragmentation peaks are observed at lower mass region (< 1600 m/z). Matrix peaks are denoted as (*).



Figure S17 Comparison of the number of repeating units on each fragments in MALDI-TOF spectrum of $PEG_{-15}(OPCB)_4$ (**6a**) and $PEG_{-15}(OPCB)_3(OH)$ (**6b**) with Na⁺ ion. Number on top of the peaks is the observed molecular mass of the signals. Red dotted line denoted 14 repeating units.



Figure S18 The UV-vis spectra of toluene and starting $PEG_{4}(OH)_{2}(1)$, $PEG_{21}(OH)_{3}(2)$ & $PEG_{15}(OH)_{4}(3)$, all recorded in toluene.











Figure S21 Full positive ionization MALDI-TOF spectrum of $PEG_{24}(OH)_3$ (7). Primary signal $[M+H]^+$ 1248 m/z, and other peaks are $[M+C_2H_4O+H]^+$ 1292 m/z, $[M+NH_4]^+$ 1264 m/z, $[M-C_2H_4O+H]^+$ 1204 m/z, $[M-(C_2H_4O)_4+H]^+$ 1072 m/z.



Figure S22 The FTIR spectrum of PEG₂₄(OPCB)₃.