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Supporting Information

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High electron mobility and tuneable glass transition temperature in fullerene - functionalized polynorbornenes

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Supplementary Figures and Table

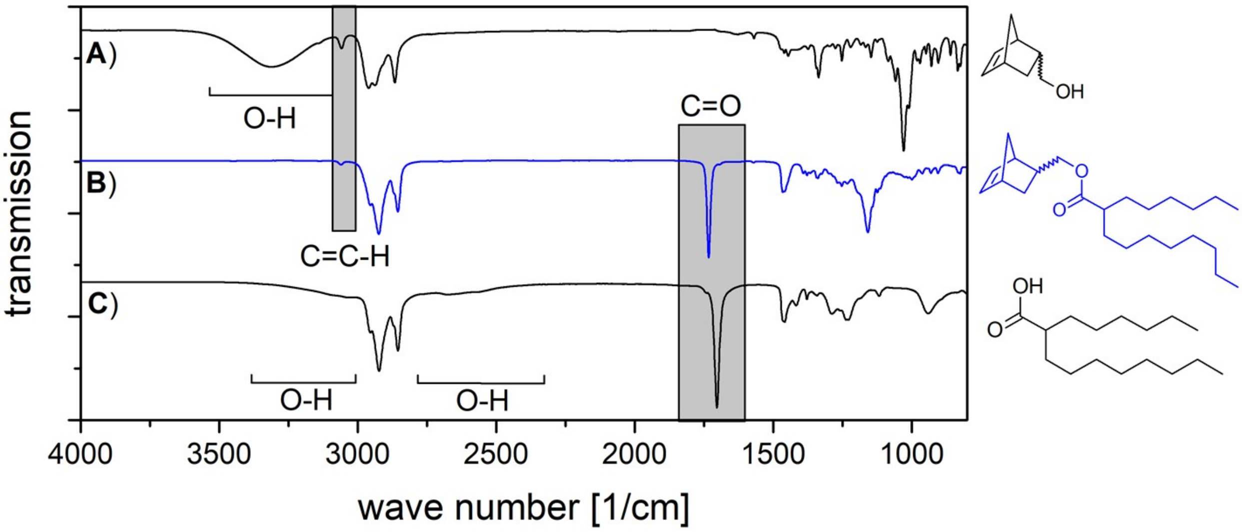


Figure S1: FT-IR spectra of the esterification educts 5-norbornene-2-methanol (**A**), isopalmitic acid (**C**), and product isopalmitic acid norbornenyl ester (**B**). Upon reaction, the educt hydroxy stretching vibrations disappear and a shift in the carbonyl stretching vibration can be observed.

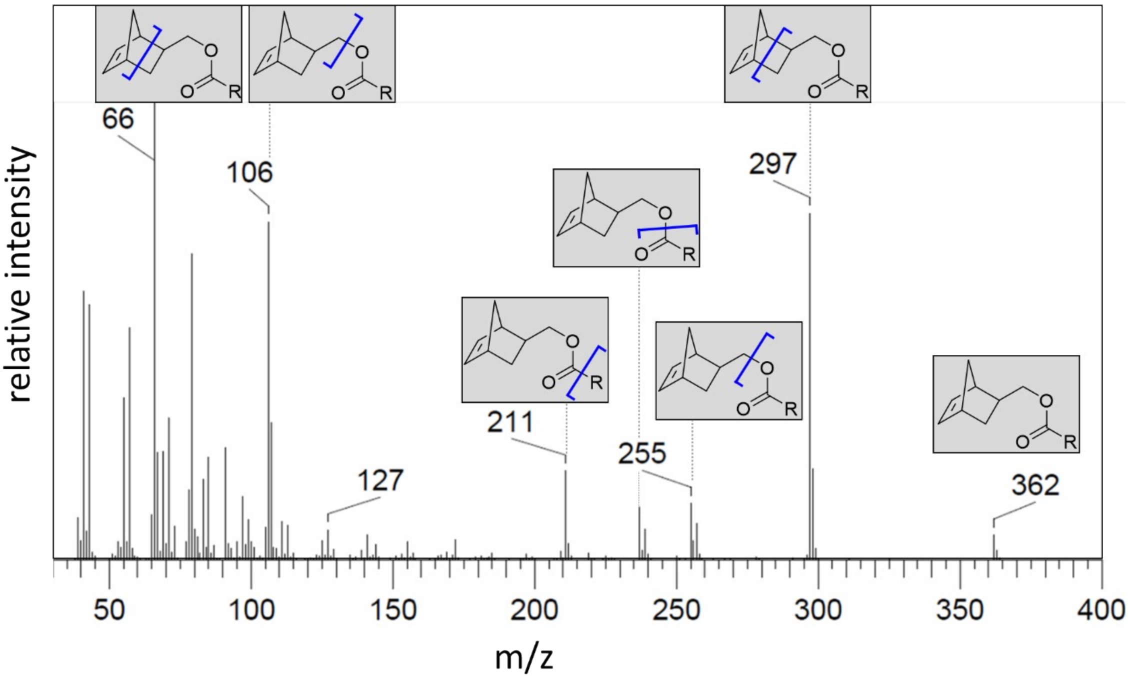


Figure S2: DIP mass spectrum of purified isopalmitic acid norbornenyl ester.

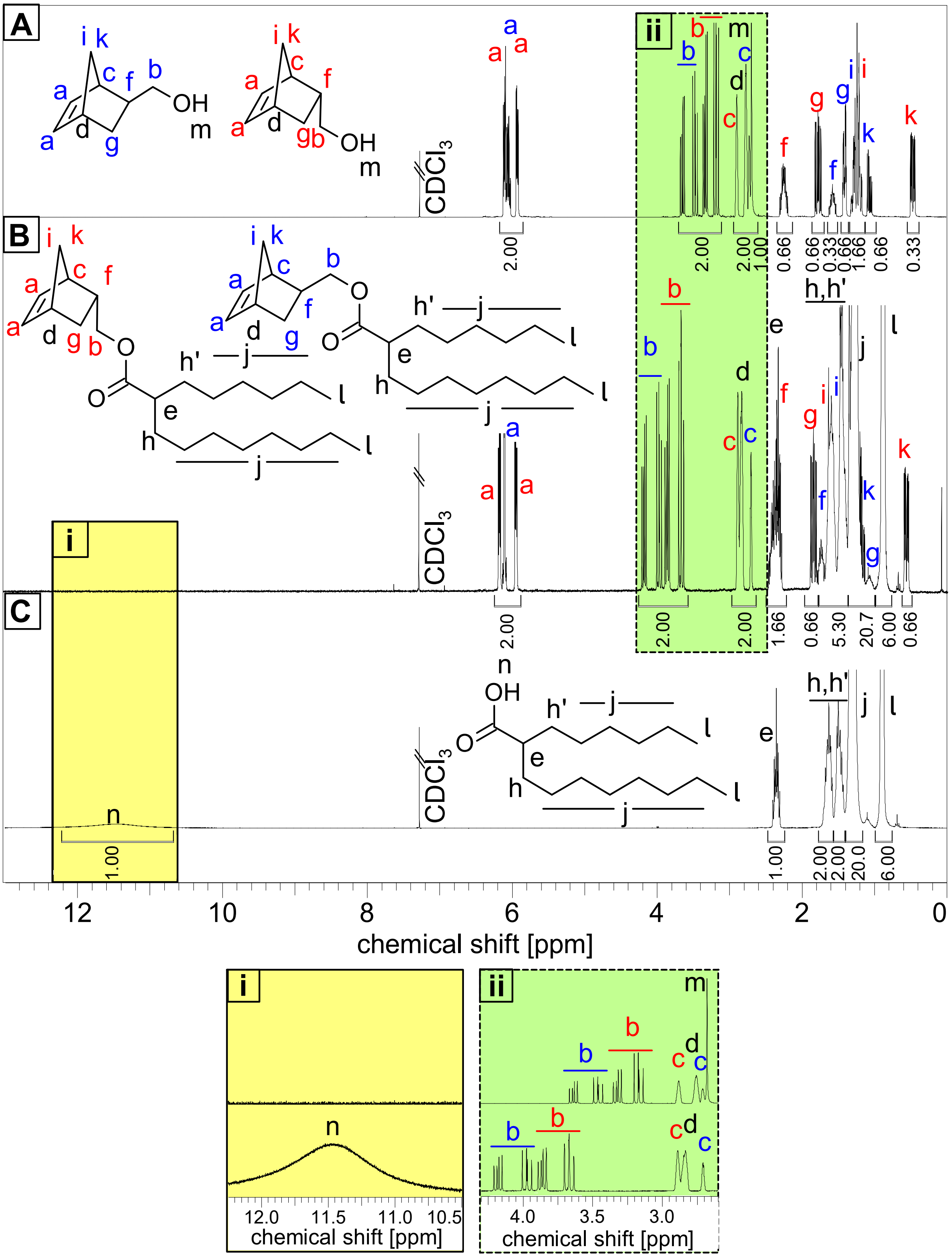


Figure S3: ¹H-NMR spectra of the esterification educts 5-norbornene-2 methanol (**A**), isopalmitic acid (**C**), and the product isopalmitic acid norbornenyl ester (**B**) with assigned signals. The reaction success can be observed on the disappearance of the acidic proton highlighted in **box i**. Further, the alcohol proton disappears and the signals of methylene protons neighboring the ester functionality are lowfield shifted, which is highlighted in **box ii**. Spectra were recorded in $CDCl_3$ at room temperature.

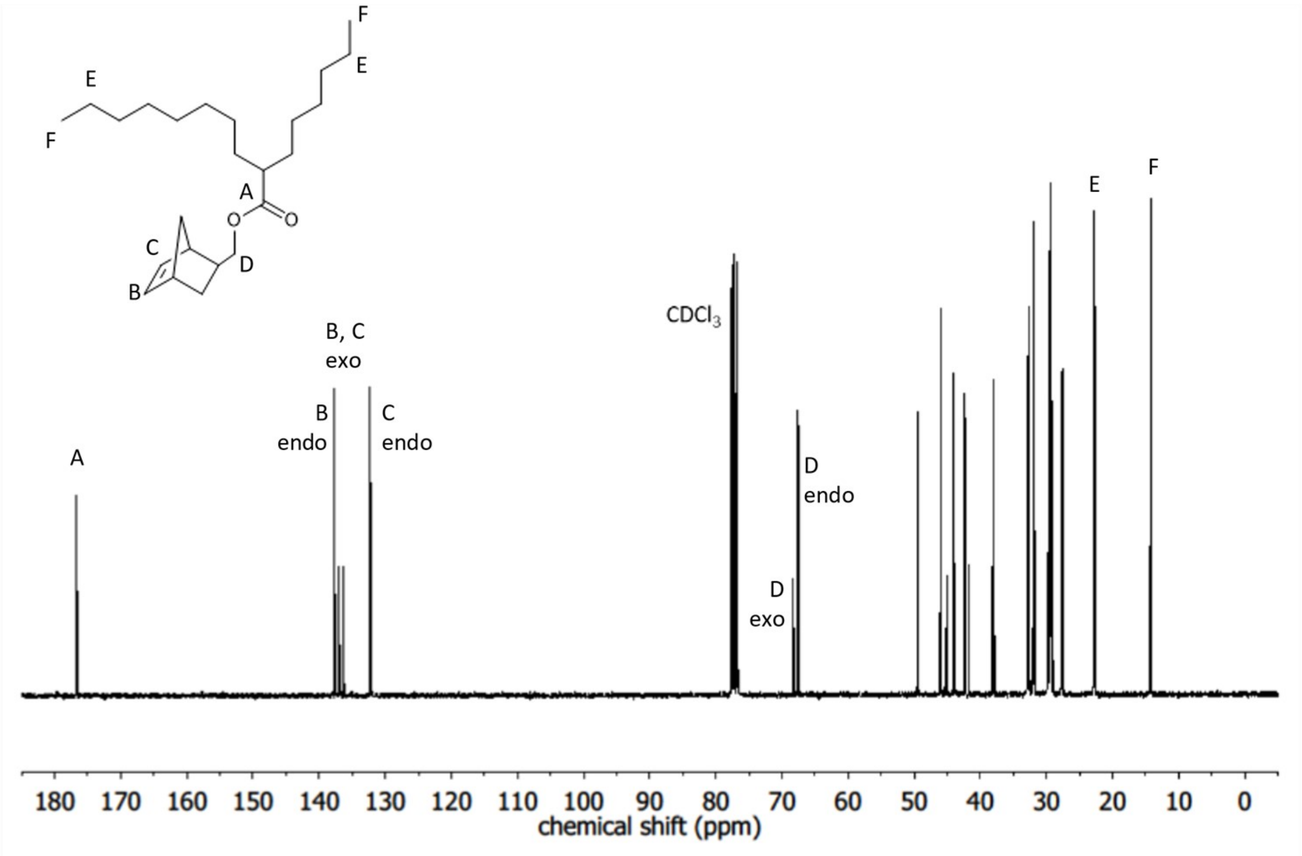


Figure S4: 13C- NMR spectrum of the alkyl functionalized monomer Alk-Nb. Note that the presence of different isomers effects signal splitting.

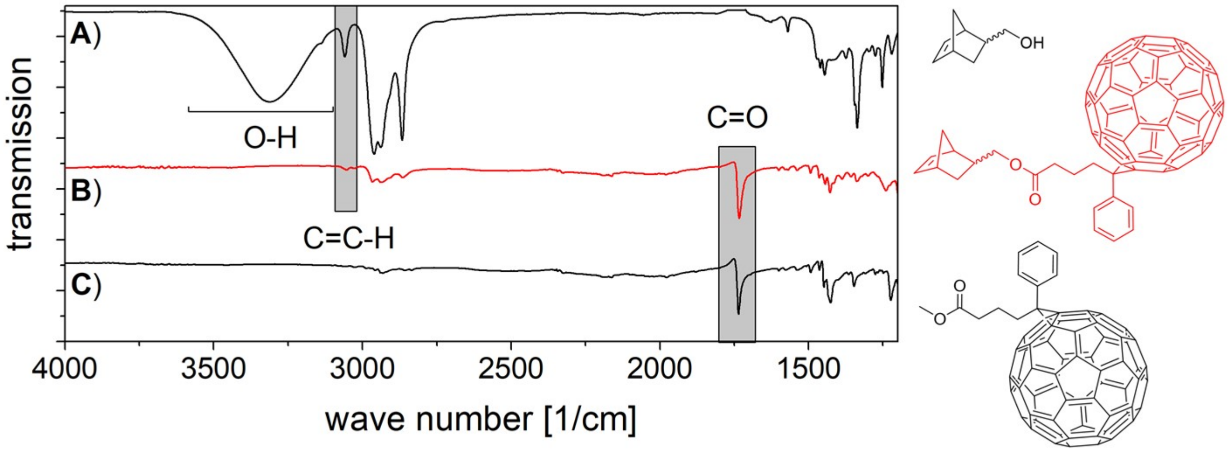


Figure S5: FT-IR spectra of the transesterification educts 5-norbornene-2-methanol (**A**), PCBM (**C**), and product PCB-Nb (**B**). Upon comparison of Nb-CH$_2$OH and the product, the disappearance of the hydroxy stretching vibration at $\tilde{\nu}_{OH}$ = 3000 cm^{-1} – 3600cm^{-1} is apparent.

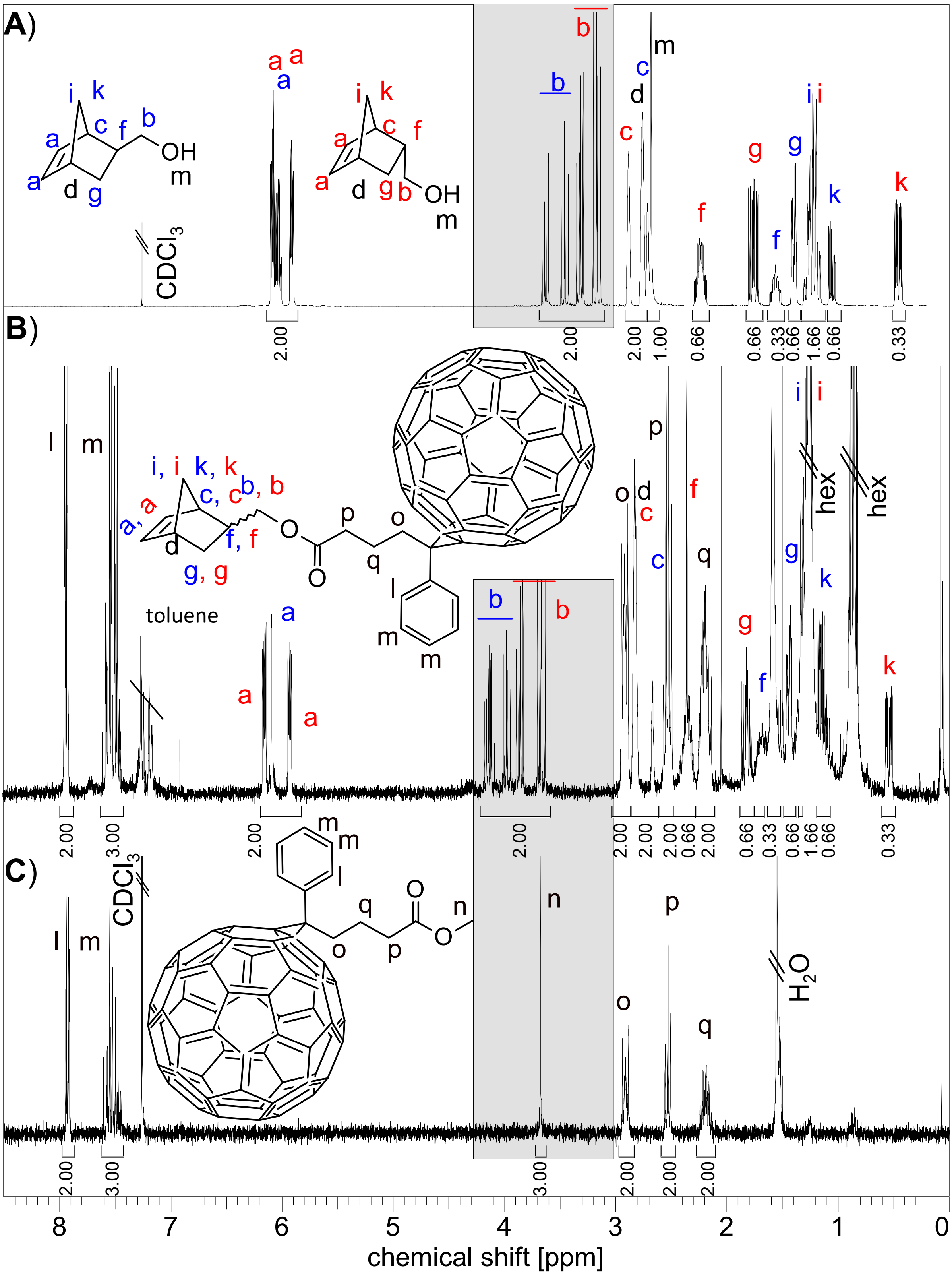


Figure S6: ^{1}H-NMR spectra of the transesterification educts 5-norbornene-2 methanol (**A**), PCBM (**C**), and the product PCB-Nb (**C**) with assigned signals. The reaction success can be seen on the disappearance of the hydroxy proton of Nb-CH_2OH at 3.65 ppm. Further, the signals of methylene protons neighbouring the ester functionality experience an increase in chemical shift. Spectra were recorded in $CDCl_3$ at room temperature. Spectra (**Figure S6**, (**A**) and (**C**)) and the ^{1}H NMR spectrum of the product (**Figure S6**, (**B**)). All product protons can be assigned to a signal in the spectrum. Further, the methylene protons of 5-norbornene-2-methanol at δ = 3.7 ppm – 3.1 ppm experience a deep field shift to δ = 4.2 ppm – 3.6 ppm upon esterification. The complete removal of the alcohol educt can be proven by the absence of associated methylene signals. Further, the methyl substituent of the ester is split during the reaction and replaced by the desired norbornenyl substituent. Thus, the absence of the methyl signal of PCBM at δ = 3.7 ppm in the product spectrum is indicative of its quantitative removal.

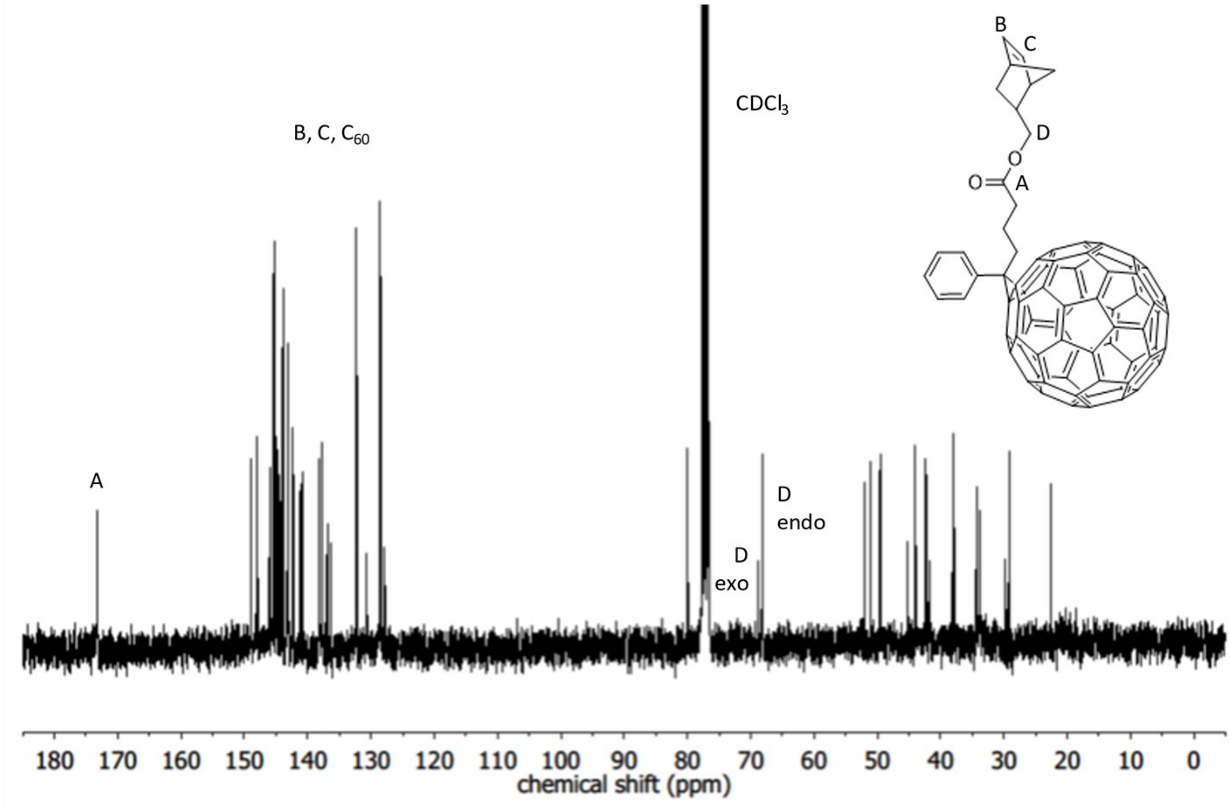


Figure S7: ^{13}C- NMR spectrum of the fullerene-functionalized monomer PCB-Nb. Note that the presence of different isomers effects signal splitting.

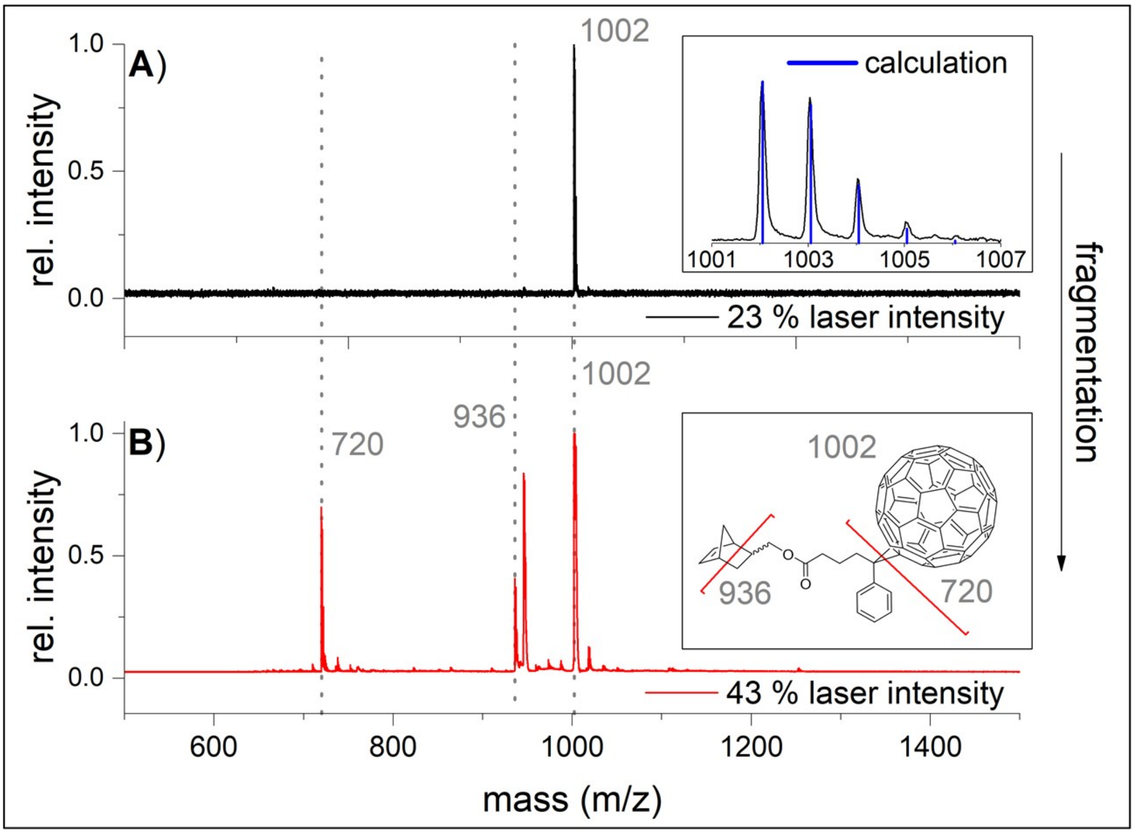


Figure S8: MALDI-ToF spectra of the purified reaction product PCB-Nb. **A**) At low laser intensities, only the [M]$^-$ signal is detected, which suggests high purity. **B**) Upon laser intensity increase, fragmentation begins, which results in the detection of characteristic product fragments at lower molecular weight. The weight ratio of sample: matrix (dithranol) was 1 : 20 without salt addition. The spectra were recorded as sum of 500 scans in negative ion mode with the indicated laser intensities.

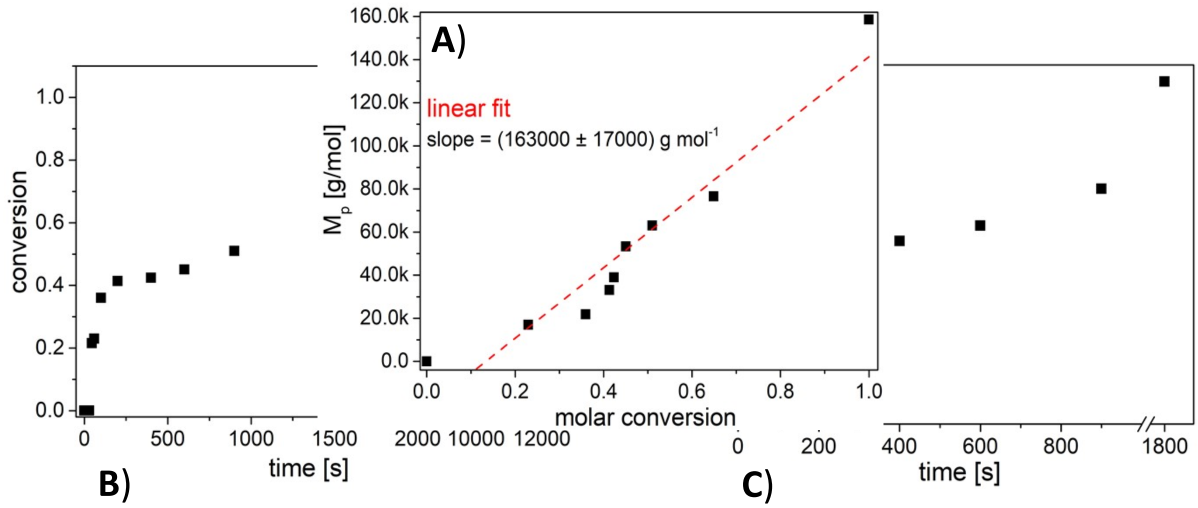


Figure S9: Dependence of the number average molecular weight (**A**), peak molecular weight (**B**), and dispersity (**A**) on the monomer conversion during the copolymerization yielding P(PCB-Nb)30. The conversion was determined by ^{1}H-NMR spectroscopy, the molecular weight by SEC (eluent: THF + 0.25 wt. % TBAB, PS calibration). The respective samples were taken from the active polymerization and quenched in ethyl vinyl ether without further purification. For comparison, conversion and of ln([M]$_0$/[M]$_t$] are shown again in (**C**) and (**D**).

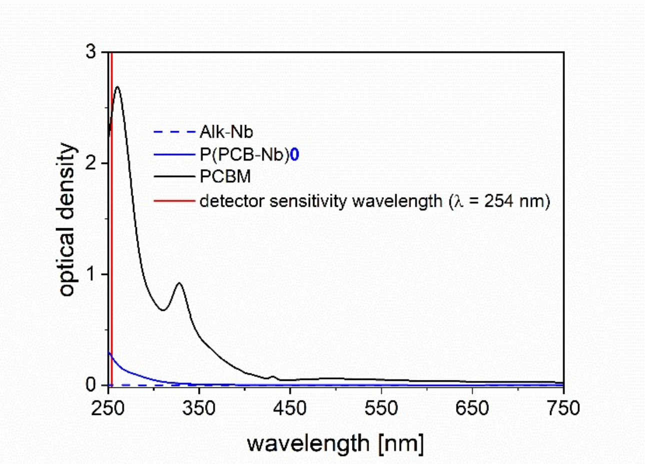


Figure S10: **A**) Absorption of the monomer Alk-Nb, P(Alk-Nb), and PCBM in the visible and ultraviolet wavelength region. The red line highlights the wavelength λ = 254 nm, which is used for detection in SEC measurements in **Figure 2** (c).

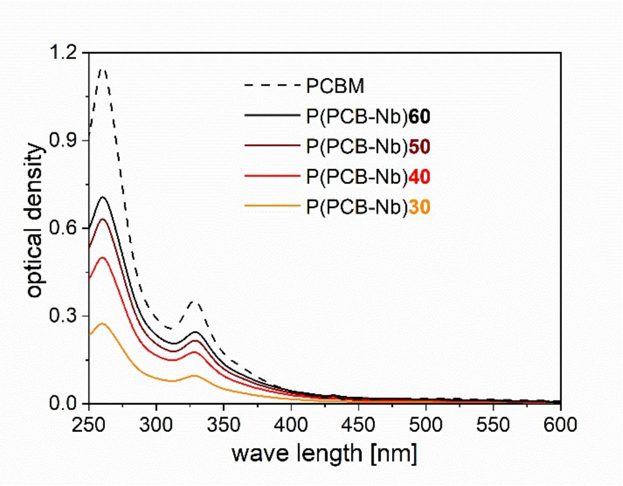


Figure S11: **A**) Quantitative UV-Vis absorption spectra of the four fullerene-grafted copolymers (solid lines) and the chromophore PCBM (dashed line) in chloroform solutions with concentrations of c = 10 mg/L. The absorption bands are congruent, due to the identical chromophore. The optical density is predominantly determined by the fullerene content on the individual materials.

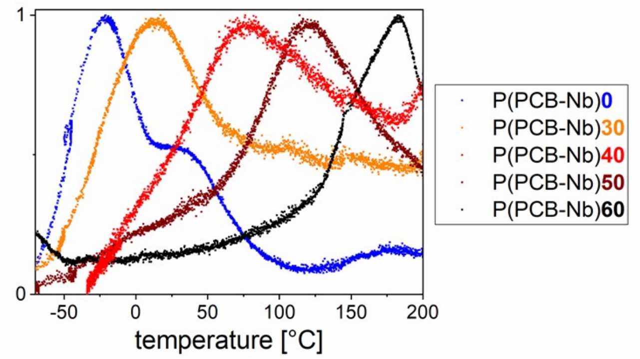


Figure S12: Loss tangent (tan δ) cooling curves determined by DMTA (under N_2 atmosphere with a heating and cooling rate of 2 K/min and an oscillation frequency of 2 Hz) for polymers with different fullerene contents. The glass transition temperature is extracted from the peak maxima. A clear correlation between the C_{60} content and the thermal transition can be seen in the heating and cooling curves.

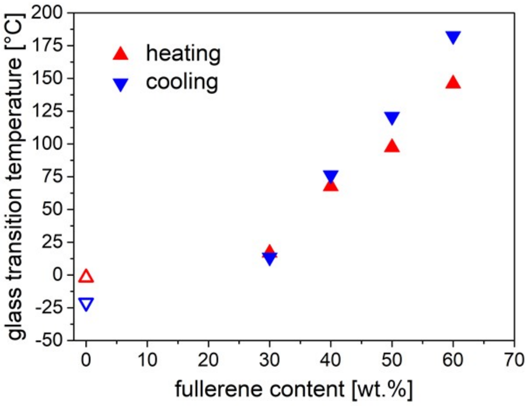


Figure S13: Glass transition temperatures of the synthesized poly(norbornene) copolymers dependent on the fullerene weight content.

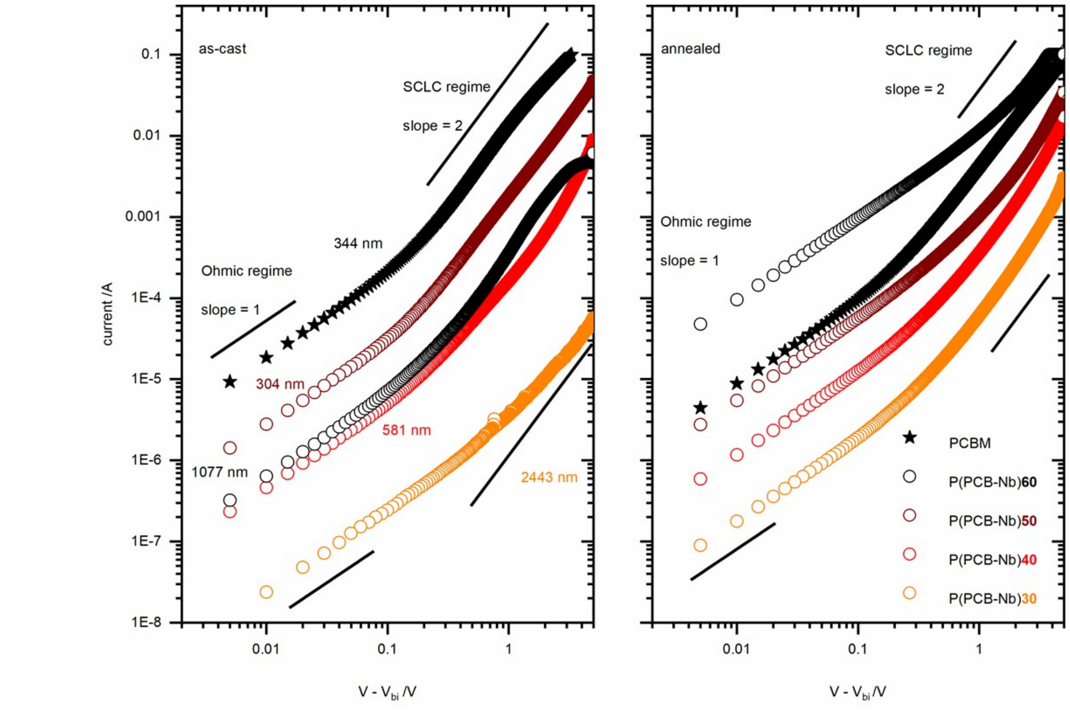


Figure S14: Double logarithmic plot of the IV measurements used for SCLC characterization of the polymers P(PCB-Nb)30 – P(PCB-Nb)60 in the pristine and annealed state. The transition from the ohmic regime with $I \propto V$ to the space charge limited regime with $I \propto V^2$ can be seen.

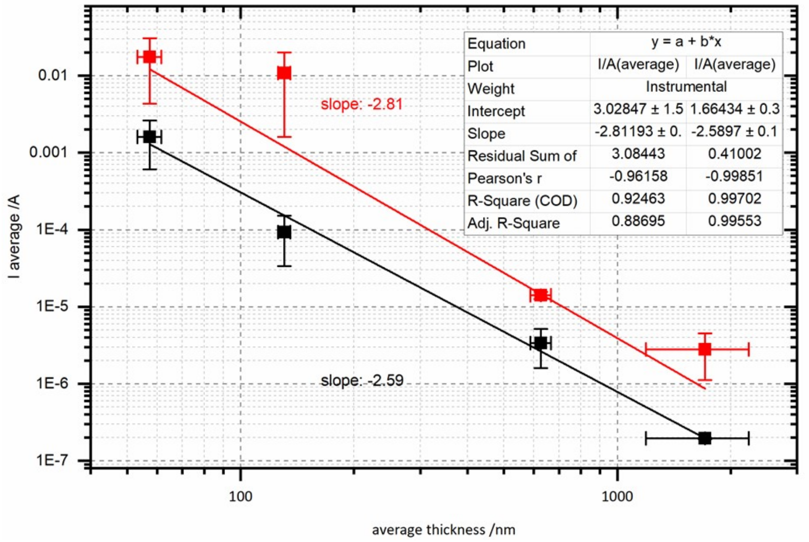


Figure S15: Current and thickness averaged over several P(PCB-Nb)**50** containing SCLC devices before and after annealing to demonstrate the required I ∝ d^{-3} dependence, derived from the MURGATROYD equation.

Table S1: Molecular weight and dispersity of the copolymers **P(PCB-Nb)30** - **P(PCB-Nb)60** determined by the complementary methods SEC and MALDI-ToF.

Copolymer	Target C_{60} content	Target M_n	M_n (SEC, $CHCl_3$)	Đ	M_p (MALDI-ToF)
P(PCB-Nb)30	30 wt.%	47 kg/ mol	43.9 kg/mol	2.0	47 kg/ mol
P(PCB-Nb)40	40 wt.%	35 kg/ mol	34.5 kg/mol	2.2	49 kg/ mol
P(PCB-Nb)50	50 wt.%	28 kg/ mol	15.5 kg/mol	1.3	31 kg/mol
P(PCB-Nb)60	60 wt.%	23 kg/ mol	11.2 kg/mol	1.3	24 kg/mol

Table S2: Glass transition temperatures of the synthesized fullerene grafted polymers with C_{60} contents between 0 and 60 wt.%.

Material	Fullerene content	T_g (DMTA, heating)	T_g (DMTA, cooling)
P(PCB-Nb)0	0 wt. %	-2.0 °C	-21.1
P(PCB-Nb)30	30 wt.%	16.8 °C	13.5
P(PCB-Nb)40	40 wt.%	67.6 °C	76.2
P(PCB-Nb)50	50 wt.%	97.3 °C	120.9
P(PCB-Nb)60	60 wt.%	145.9 °C	182.4

Materials and methods

Chemicals were used as received, if not instead otherwise noted.
Ethyl vinyl ether (0.1 % KOH as stabilizer, 99 %) and 3rd generation GRUBBS catalyst, were purchased from Sigma Aldrich. *o*-Dichlorobenzene (99.8 %, extra dry, AcroSeal®) was bought from Acros Organics. Methanol (99.9 %) and tetrahydrofuran (99.9 %) and thionyl chloride were received from VWR chemicals. PCBM was purchased from Solaris Chem Inc. 5-norbornene-2-methanol and isopalmitic acid were purchased from TCI Chemicals. Deuterated chloroform ($CDCl_3$) was purchased from Deutero. The remaining solvents were distilled in-house prior to use.

^{1}H NMR spectroscopy

^{1}H NMR spectra (with 64 – 2048 scans) were recorded using a Bruker Avance 250 spectrometer at a working frequency of 300 MHz. Chemical shifts are given in ppm and coupling constants (J) in Hertz (Hz). The spectra were referenced to the residual solvent peak of $CDCl_3$ (δ = 7.26 ppm for ^{1}H spectra and δ = 77.16 ppm for ^{13}C spectra).

Thermogravimetric analysis (TGA)

TGA thermograms were recorded using a Mettler Toledo TGA/DSC 3+. Measurements were conducted under N_2 atmosphere between 30 °C–700 °C at a heating rate of 10 K/min. Specimens (between 1 and 7 mg) were filled into Al_2O_3 crucibles (volume 70 µL).

Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-ToF MS)

MALDI-ToF measurements were performed using a Bruker Reflex II mass spectrometer. A mixture of 1,8-dihydroxy-9,10-dihydroanthracene-9-one (dithranol) and potassium trifluoro-acetate (KTFA) was used as the matrix at a ratio of 50/1/1 (matrix/sample/salt). If not state otherwise explicitly.

Attenuated Total Reflection Fourier-Transform Infrared Spectroscopy (ATR-FTIR)

IR spectra were recorded from solids on a Perkin Elmer Spectrum 100 FTIR spectrometer in attenuated total reflection (ATR) mode.

Dynamic Mechanical Thermal Analysis (DMTA)

DMTA measurements were performed on a Mettler ToledoDMA1 Star eSystem with a heating rate of 2 K/min and an oscillation frequency of 2.000 Hz. The measurements were performed in a single cantilever setup in a titanium sample holder. The measurement range was between T = -100 °C and T = 200 °C.

Ultraviolet-visible (UV-Vis) spectroscopy

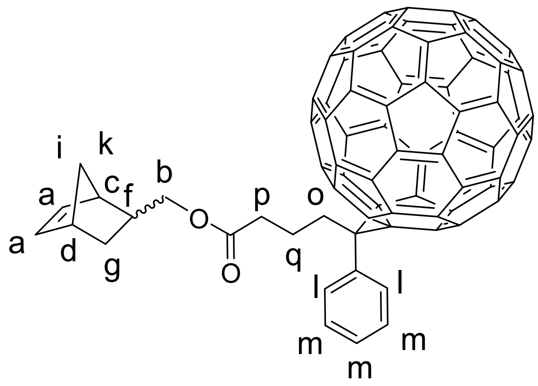
UV-vis spectra were recorded on a Hitachi U-3000 spectrophotometer using quartz cuvettes with a path length of 1 cm. Prior to sample measurements, a background measurement of the pure solvent, chloroform, was performed and subtracted from the following measurements.

SCLC Device fabrication

Electron-Only Space-charge-limited-current (SCLC) devices in diode configuration for determination of bulk electron mobilities. The stacks (glass/FTO/ZnO/active material/Ca/Al) included 40 nm ZnO layers, established via a sol-gel method. After deposition of the blocking layer, active materials were knife coated from 10 g/L $CHCl_3$ solutions at 60 °C under inert conditions.
The observation of a $I \propto V^2$ and $I \propto L^{-3}$ dependency, that can be derived from the MOTT GOURNEY Law, are required for the applicability of the used SCLC analysis. Square voltage dependence is shown for all materials before and after annealing in **Figure S14**, the thickness dependency for P(PCB-Nb)50 in **Figure S15**. It was assumed, that the thickness dependence applies for all materials, as they share the same electrochemically active chromophore.

Synthesis

(5-Norbornenyl)methyl phenyl-C_{61}-butanecarboxylate (PCB-Nb)



Chemical Formula: $C_{79}H_{22}O_2$
Molecular Weight: 1003.04 g/mol

In three separate dried schlenk flasks, PCBM (1 eq.), 5-norbornene-2-methanol (2 eq.) and NaH (60 wt. % dispersion in mineral oil, 2.4 eq.) are dissolved in *o*-dichlorobenzene. (PCBM solution: 18.2 mL/mmol; alcohol solution: 2.3 mL/mmol; NaH solution 1.9 mL/mmol). Residue water is then removed under stirring *in vacuo* for 15 min, followed by backfilling of the flasks with argon. The NaH dispersion is then added to the stirred alcohol solution resulting in gas evolution. When no reaction can be observed, the flask is evacuated and backfilled with argon and the PCBM solution is added under continuous stirring. The reaction progress can be monitored by thin layer chromatography (Toluene, R_f(PCBM) = 0.66, R_f(PCB-Nb) = 0.83, R_f(PCBA) = 0). After two hours, almost full conversion is reached, and the reaction is terminated by three washings with aqueous HCl (2 mol%). The organic phase is washed twice with saturated $NaHCO_3$ solution and once with saturated brine. The solution is concentrated *in vacuo* and precipitated in methanol three times, followed by filtration over a short AlOx n column. Column chromatography (Silica, toluene: cyclohexane = 7 : 3) yields the product, a black solid in the second fraction.

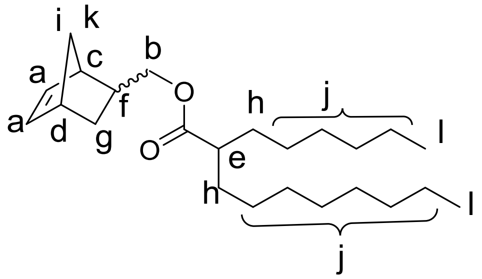
Yield: 46 %

FT-IR: C-H: 2920 cm^{-1}, 2850 cm^{-1}, C=O: 1722 cm^{-1}.

^{1}H-NMR ($CDCl_3$, 300 MHz): δ [ppm] = 7.9 (m, 2H, H_l), 7.5 (m, 3H, H_m), 6.1 (m, 2H, H_a), 4.2 – 3.6 (m, 2H, H_b), 2.9 (m, 2H, H_o), 2.7 – 2.8 (d, 2H, H_c, H_d), 2.5 (m, 2H, H_p), 2.4 (m, 0.7H, $H_{f\text{-}endo}$), 2.2 (m, 2H, H_q), 1.8 (m, 0.7H, $H_{g\text{-}endo}$), 1.7 (m, 0.3H, $H_{f\text{-}exo}$), 1.4 (m, 0.7H, $H_{g\text{-}exo,}$), 1.3 (m, 1H, H_i), 1.1 (dm, 0.3H, $H_{k\text{-}exo}$), 0.6 (dm, 0.7H, $H_{k\text{-}endo}$).

MS: m/z (relative intensity): 1002 (M^-)

(5-Norbornenyl)methyl 2-hexyldecanoate (Alk-Nb)



Chemical Formula: $C_{24}H_{42}O_2$
Molecular Weight: 362.60

In a dry schlenk flask 2-hexyldecanoic acid (1 eq.) is stirred under high vacuum to remove trace water. 5 min after no gas evolution is observable, thionyl chloride (2.7 eq.) is added. Evolving gases are bubbled through wash flasks with aqueous NaOH solution. The temperature is slowly increased to 80 °C and then maintained for 90 min. Unreacted thionyl chloride is then removed by vacuum distillation. Then the solution is cooled to 0 °C and pyridine (0.68 mmol/mL 2-hexyldecanoic acid) is added and cooled as well. 5-norbornene-2-methanol is added, which resulted in the solution to turn turbid immediately. The reaction was allowed to stir over night under reflux (115 °C) where the solution turns clear again. Upon cooling, crystals of pyridinium hydrochloride form and are removed by gravity filtration. The organic phase is washed twice with HCl (1M, aq.), $NaHCO_3$ (saturated) and brine. The solvent is removed under reduced pressure. The product is isolated *via* column chromatography (silica, hexane : ethyl acetate = 30 : 1, first fraction). Solvents are removed *in vacuo* for 48 h to yield a colorless oil.

Yield: 74 %.

FT-IR: C=C-H: $\tilde{\nu}$ = 3060 cm^{-1}, C-C-H: $\tilde{\nu}$ = 2920 cm^{-1}, $\tilde{\nu}$ = 2850 cm^{-1}, C=O: $\tilde{\nu}$ = 1730 cm^{-1}.

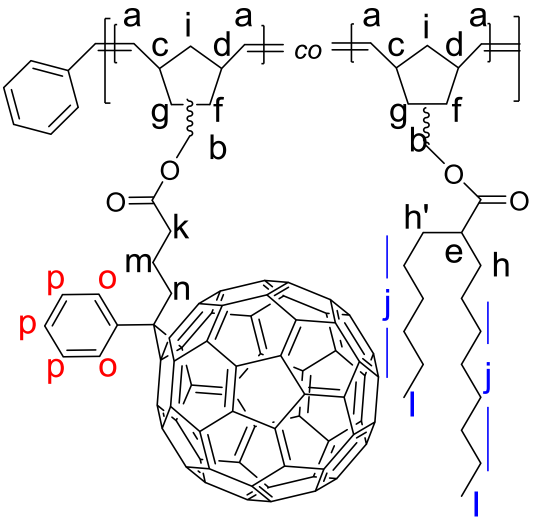
^{1}H-NMR ($CDCl_3$, 300 MHz): δ [ppm] = 6.04 (ddd, 1.3H, $H_{a/endo}$), 6.09 (m, 0.7H, $H_{a/exo}$), 4.17 (dd, 0.35H, $H_{b/exo}$), 3.96 (dd, 0.35H, $H_{b/exo}$), 3.85 (dd, 0.65H, $H_{b/endo}$), 3.66 (dd, 0.65H, $H_{b/endo}$), 2.88 (m, 0.65H, $H_{c/endo}$), 2.83 (m, 0.65H, H_d), 2.70 (m, 0.65H, $_{Hc/exo}$), 2.40 (m, 1H, H_e), 2.32 (m, 0.65H, $H_{f/endo}$), 1.84 (ddd, 0.65H, $H_{g/endo}$), 1.70 – 1.38 (dm, 4H, H_h), 1.60 (m, 0.65H, $H_{f/exo}$), 1.46 (dm, 0.65H, $H_{i/endo}$), 1.35 (dm, 0.65H, $H_{i/exo}$), 1.33 – 1.21 (m, 20H, H_j), 1.25 (m, 0.35H, $H_{k/exo}$), 1.20 (m, 0.35H, $H_{g/exo}$), 1.17 (ddd, 0.35H, $H_{g/exo}$), 0.88 (t, 6H, H_l), 0.56 (ddd, 0.65H, $H_{k/endo}$).

MS: m/z (relative intensity): 362 (M^+), 297, 256, 211, 172, 144, 106, 66.

General Procedure for Ring-Opening Metathesis Polymerization

The monomer or monomers are weighed into a dry schlenk flask under argon counter flow. And degassed *in vacuo* for 10 min. Dry *o*-dichlorobenzene (15 mL/mmol monomer) is added through a septum or under argon counter flow to the flask. Trace water and oxygen are removed under stirring *in vacuo* for 20 min. The vessel is cooled to 6 °C in a hexane/ dry ice bath. Third generation GRUBBS CATALYST is weighed into a vial with septum under inert gas atmosphere and dissolved in 1 mL dry o-dichlorobenzene. If the catalyst mass exceeded 20 mg, it was dissolved in 2 mL solvent instead. To initiate the polymerization, the catalyst is added *rapidly* and under strong stirring to the monomer solution through a syringe. During the reaction, the temperature of 6 °C is maintained. To terminate the polymerization ethyl vinyl ether (0.14 mL/mmol educt monomer) is added. After 15 minutes of stirring, the polymer is precipitated in methanol, tempered to -78 °C by an acetone/dry ice bath. The polymer is re-dissolved in chloroform and precipitated twice more in the anti-solvent at room temperature. After freeze drying from benzene, the purified polymer is yielded.

Poly((5-norbornenyl)methyl 2-hexyldecanoate-*stat*-(5-norbornenyl)methyl phenyl-C$_{61}$-butanecarboxylate)



The copolymerization reactions of (5-norbornenyl)methyl 2-hexyldecanoate and 5-norbornenyl)methyl phenyl-C$_{61}$-butanecarboxylate) are conducted according to the general procedure. Different monomer ratios are polymerized with a fixed PCB-Nb : catalyst ratio of 1 : 16.67. The (5-norbornenyl)methyl 2-hexyldecanoate equivalents *m* are varied according to **Table S3**. The monomers are dissolved *o*-dichlorobenzene and degassed *in vacuo* under stirring in a dry schlenk flask. After the catalyst is added (1 eq.), the reaction is stirred for two hours and terminated by subsequent addition of ethyl vinyl ether. After five minutes of stirring, the polymer is precipitated in methanol at -78 °C. After thawing of the o-dichlorobenzene crystals, the yellow solvent mixture is decanted from the polymer. This procedure is repeated twice, and the purified product dissolved in chloroform for storage. During the polymerization of P(PCB-Nb)30, samples were taken from the active reaction after 10 sec, 20 sec, 30 sec, 45 sec, 1 min, 100 sec, 200 sec, 400 s, 600 sec, 900 s and 1800 s and quenched immediately with ethyl vinyl ether for kinetic investigations.

Table S3: Theoretical ratio between monomers and catalyst and the real ratios.

Polymer	P(PCB-Nb)**30**	P(PCB-Nb)**40**	P(PCB-Nb)**50**	P(PCB-Nb)**60**
ratio (theoretical) [G$_3$] : [PCB-Nb] : [Nb-Alk]	1 : 16.67 : 64.18	1 : 16.67 : 36.67	1 : 16.67 : 20.17	1 : 16.67 : 9.00
ratio (real) [G$_3$] : [PCB-Nb] : [Nb]	1 : 16.67 : 66.03	1 : 16.67 : 37.66	1 : 16.67 : 19.48	1 : 16.67 : 9.17

P(PCB-Nb)**30**

Yield: 64.2 %

^{1}H-NMR (CDCl$_3$, 300 MHz): δ [ppm] = 7.9 (b, 0.4H, H$_o$), 7.5 (b, 0.63H, H$_p$), 5.5 – 5.2 (b, 2H, H$_a$), 4.2 – 3.8 (n, 2H, H$_b$), 3.2 – 1.4 (12H, H$_c$ – H$_{i,}$, H$_k$, H$_m$, H$_n$), 1.3 (b, 16.7H, H$_j$), 0.85 (t, 4.9H, H$_l$).

SEC (CHCl$_3$): M_n = 43.9 kg/mol; M_w = 85.9 kg/mol; $Đ$ = 2.0

MALDI-ToF: M_p = 47 kg/mol

TGA: $T_{d,5\%}$ = 331.2 °C

DMTA: $T_{g\ (heating)}$ = 16.8 °C, $T_{g\ (cooling)}$ = 13.5 °C

P(PCB-Nb)**40**

Yield: 68.5 %

^{1}H-NMR ($CDCl_3$, 300 MHz): δ [ppm] = 7.9 (b, 0.6H, H_o), 7.5 (b, 0.55H, H_p), 5.5 – 5.2 (b, 2H, H_a), 4.2 – 3.8 (n, 2H, H_b), 3.2 – 1.4 (12H, H_c – H_i, H_k, H_m, H_n), 1.3 (b, 16.0, H_j), 0.85 (t, 4H, H_l).

SEC ($CHCl_3$): M_n = 34.5 kg/mol; M_w = 74.8 kg/mol; $Đ$ = 2.2

MALDI-ToF: M_p = 49 kg/mol

TGA: $T_{d,5\%}$ = 325.3 °C

DMTA: $T_{g\ (heating)}$ = 67.6 °C, $T_{g\ (cooling)}$ = 76.2 °C

P(PCB-Nb)**50**

Yield: 92.3 %

^{1}H-NMR ($CDCl_3$, 300 MHz): δ [ppm] = 7.9 (b, 1.0H, H_o), 7.5 (b, 0.55H, H_p), 5.5 – 5.2 (b, 2H, H_a), 4.2 – 3.8 (n, 2H, H_b), 3.2 – 1.4 (12H, H_c – H_i, H_k, H_m, H_n), 1.3 (b, 11.9, H_j), 0.85 (t, 3.0H, H_l).

SEC ($CHCl_3$): M_n = 15.5 kg/mol; M_w = 20.2 kg/mol; $Đ$ = 1.3

MALDI-ToF: M_p = 31 kg/mol

TGA: $T_{d,5\%}$ = 333.8 °C

DMTA: $T_{g\ (heating)}$ = 97.3 °C, $T_{g\ (cooling)}$ = 120.9 °C

P(PCB-Nb)60

Yield: 87.4 %

^{1}H-NMR ($CDCl_3$, 300 MHz): δ [ppm] = 7.9 (b, 1.3H, H_o), 7.5 (b, 0.55H, H_p), 5.5 – 5.2 (b, 2H, H_a), 4.2 – 3.8 (n, 2H, H_b), 3.2 – 1.4 (12H, H_c – H_i, H_k, H_m, H_n), 1.3 (b, 16.0, H_j), 0.85 (t, 2.1H, H_l).

SEC ($CHCl_3$): M_n = 11.2 kg/mol; M_w = 15.1 kg/mol; $Đ$ = 1.3

MALDI-ToF: M_p = 24 kg/mol

TGA: $T_{d,5\%}$ = 347.3 °C

DMTA: $T_{g\ (heating)\ =}$ 145.9 °C, $T_{g\ (cooling)}$ = 182.4 °C