

Supporting Information for: Investigating the dielectric properties and exciton diffusion in C₇₀ derivatives

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Contents

1	Synthesis	S-3
1.1	Methanofullerenes	S-3
1.2	Bingel adducts	S-4
2	NMR spectra	S-7
3	Neat material properties	S-12
3.1	Average distance between excitons	S-14
4	Blended films	S-16
4.1	Monte-Carlo Simulations	S-16

4.2	UV-Vis spectra	S-18
4.3	Time-resolved PL	S-19
5	AFM images	S-22
5.1	Blends with TPTPA as quencher	S-22
5.2	Blends with BDT-PhTEG and OT	S-23
6	Dielectric properties	S-25
6.1	Impedance spectroscopy	S-25
6.2	Ellipsometry	S-26
7	Differential scanning calorimetry	S-28

1 Synthesis

C₇₀ and [70]PCBM were purchased at Solenne B.V. TPTPA was purchased from LumTec Corp. and used as received. The synthesis of OT and BDT-PhTEG is described elsewhere. ¹H NMR was performed on an Oxford NMR AS400 or an Agilent Technologies 400/54 NMR machine and ¹³C NMR was performed on an Agilent Technologies 400/54 NMR or a Bruker Avance 600 MHz instrument. IR measurements were carried out with a Thermo Scientific Nicolet iS50 FT-IR.

1.1 Methanofullerenes

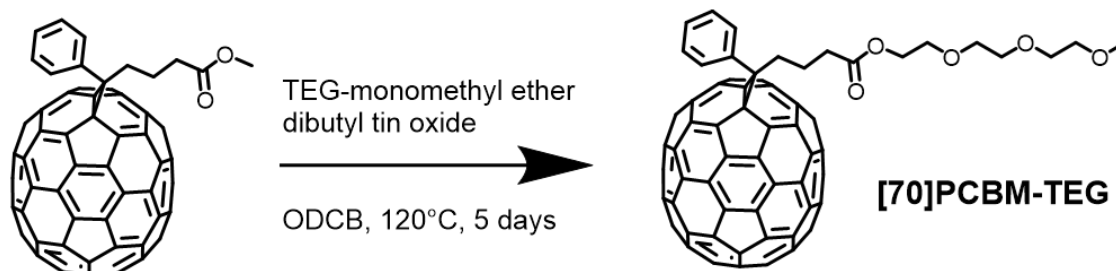


Figure S1: Synthesis of [70]PCBM-TEG

[70]PCBM-TEG: Synthesis was adapted from the literature procedure.¹ To an oven-dried 100 ml flask under nitrogen, [70]PCBM (200 mg, 0.20 mmol), triethylene glycol monomethyl ether (0.58 ml, g, 3.6 mmol), dibutyltin oxide (15 mg, 0.06 mmol) and anhydrous *o*-dichlorobenzene (20 mL) were added. The reaction mixture was heated to 120°C and stirred under N₂ for 6 days. The solvent was evaporated in vacuo, and the crude residue was dissolved in toluene, and purified using column chromatography (silica, 10% THF in toluene). The fractions containing product were collected and further purified on a second column (3:2 chloroform/ethyl acetate). The pure fractions were collected, and the resulting solid was dissolved in a minimum amount of chloroform (CHCl₃) and precipitated by adding methanol and then washed 2 x with methanol, 1 x with pentane and dried in the vacuum oven at 40°C overnight. This resulted in [70]PCBM-TEG as a mixture of isomers (177 mg, 75%). ¹H NMR (600 MHz, CDCl₃) δ 7.91 (s, 2H), 7.53 (h, J = 7.5 Hz, 2H), 7.46 – 7.38 (m, 1H), 4.26 – 4.20 (m, 2H), 3.70 – 3.68 (m, 2H), 3.66 (s, 4H), 3.65 – 3.63 (m, 2H), 3.57 – 3.53 (m, 2H), 3.38 (s, 3H), 2.54 – 2.47 (m, 2H), 2.48 – 2.41 (m, 2H), 2.23 – 2.05 (m, 2H). ¹³C NMR (151 MHz, CDCl₃) δ 173.14, 156.13, 155.42, 152.30, 152.08, 151.64, 151.36, 151.29, 151.04, 150.99, 150.74, 150.68, 149.58, 149.54, 149.36, 149.34, 149.29, 149.27, 148.74, 148.71, 148.67, 148.57,

148.47, 148.18, 148.12, 148.06, 147.72, 147.68, 147.58, 147.52, 147.18, 147.01, 146.45, 146.25, 146.08, 145.97, 145.80, 145.04, 144.66, 144.24, 144.08, 144.03, 143.90, 143.78, 143.48, 143.39, 142.79, 142.65, 141.89, 141.75, 141.57, 141.10, 140.31, 139.44, 139.06, 138.07, 137.44, 134.16, 133.99, 132.99, 132.97, 131.76, 131.06, 130.92, 130.89, 130.81, 130.58, 128.69, 128.36, 72.09, 72.04, 70.78, 70.75, 70.73, 69.96, 69.28, 63.84, 59.24, 36.06, 34.24, 34.04, 21.81. HRMS m/z calculated for $[C_{88}H_{26}O_5H]^+$: 1163.1859, found: 1163.1881. UV-Vis: $\lambda_{max}(CHCl_3)[nm] = 357$ ($\epsilon [M^{-1}cm^{-1}]$ 27000), 373 (29000), 401 (21400), 462 (23200), $\sim 540inf$, $\sim 660inf$ (1700).

1.2 Bingel adducts

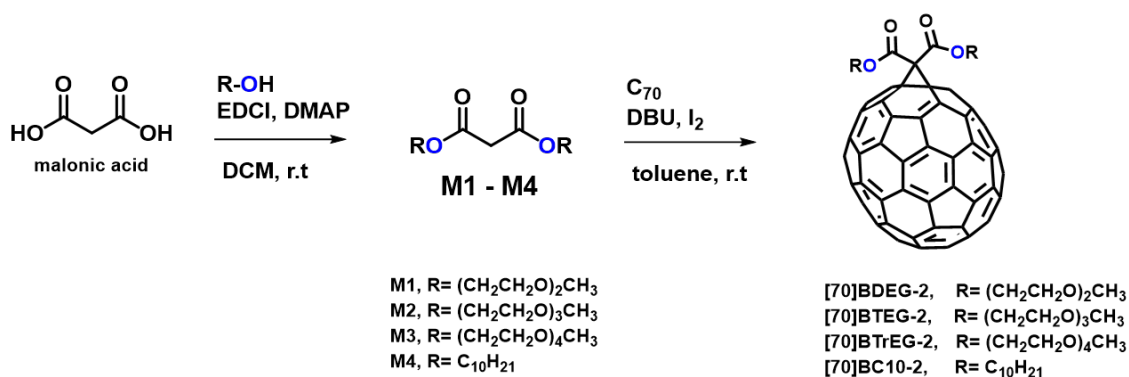


Figure S2: Synthetic route for the Bingel adduct fullerene derivatives [70]BDEG-2, [70]BTEG-2, [70]BTrEG-2 and [70]BC10-2.

Malonate precursors M1-M3 were prepared according to a previously reported procedure.²

bis(decyloxy) malonate (M4): The same synthesis conditions were used as for M1-M3. Malonic acid (0.7288 g, 7 mmol), 4-dimethylaminopyridine (DMAP) (0.1724 g, 1.4 mmol) and 1-decanol (2.216 g, 14 mmol, 2.7 ml) were added subsequently to 40 mL anhydrous DCM under a nitrogen atmosphere. *N*-Ethyl-*N'*-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI) (2.6857, 14 mmol) was added bit by bit and the yellow solution was stirred at room temperature for 24 h. The reaction mixture was washed 3 x with 20 mL 1M HCl. The aqueous phase was then extracted with 10 mL DCM, and the combined organic phases washed with 15 mL sat $NaHCO_3$ solution and dried over Na_2SO_4 . The crude was purified by column chromatography (silica, 5:1 hexane/ethyl acetate) giving the pure product as a transparent liquid (1.3466 g, 50%). Some small impurities were seen

in the NMR spectrum, however the compound was used without further purification in the next step. ^1H NMR (400 MHz, CDCl_3) δ 4.13 (t, $J = 6.8$ Hz, 4H), 3.36 (s, 2H), 1.63 (q, $J = 7.0$ Hz, 4H), 1.28 (d, $J = 17.2$ Hz, 28H), 0.88 (t, $J = 6.7$ Hz, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.86, 65.84, 41.87, 32.03, 29.68, 29.66, 29.45, 29.37, 28.62, 25.95, 22.82, 14.25.

General procedure for synthesis of the C_{70} Bingel adducts: In an oven dried flask under nitrogen, C_{70} (0.5 mmol) was dissolved in anhydrous toluene (250 ml). N_2 was bubbled through the solution for 15 minutes, after which the desired malonate (0.5 mmol) in 4 mL anhydrous toluene, I_2 (0.5 mmol) and DBU (1.1 mmol) were added. The reaction flask was covered with aluminum foil and the mixture was stirred at room temperature for 24 h. The reaction mixture was poured directly onto a silica gel column (toluene) and any unreacted C_{70} was eluted using toluene. Then, the eluent polarity was increased by adding ethanol or tetrahydrofuran (THF) to the toluene and the product was eluted off the column. After evaporation of the solvent, an oily black residue was obtained. The residue was then dissolved in a minimum amount of CHCl_3 and transferred to a centrifuge tube. Methanol was added and the mixture sonicated for 1-3 min and centrifuged at 4000 rpm for 15 min. The supernatant was decanted and the procedure was repeated, and then the solid was further washed 1 x with methanol and 3 x with pentane. The resulting pellet was dried in a vacuum oven at 40°C overnight and the C_{70} Bingel adducts were obtained as a black powder.

[70]BDEG-2: Synthesis according to the general procedure for C_{70} Bingel adducts: C_{70} (0.417 g, 0.50 mmol, M1 (0.159 g, 0.52 mmol), I_2 (0.0670 g, 0.26 mmol) and DBU (0.16 mL, 1.1 mmol). Reaction time was 24 h. Unreacted C_{70} : 0.27 g, 0.32 mmol. Eluent for column chromatography: 20% THF in toluene. [70]BDEG-2 was obtained as a black powder (110 mg, 19%). ^1H NMR (400 MHz, CDCl_3) δ 4.61 (t, 4H), 3.87 (t, 4H), 3.73 – 3.66 (m, 4H), 3.60 – 3.52 (m, 4H), 3.38 (d, $J = 0.6$ Hz, 8H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.86, 155.55, 151.82, 151.79, 151.63, 151.17, 151.04, 149.80, 149.72, 149.57, 149.19, 149.03, 148.97, 148.93, 148.08, 147.98, 147.76, 147.46, 146.92, 146.40, 146.37, 145.34, 144.40, 144.30, 143.99, 143.33, 143.29, 142.75, 142.10, 141.30, 137.38, 134.01, 133.28, 131.39, 131.36, 131.27, 102.81, 77.80, 77.48, 77.16, 72.43, 71.16, 69.22, 66.74, 59.62, 1.49. FT-IR (cm^{-1}): 674.64, 691.96, 707.78, 726.29, 741.63, 751.53, 762.52, 794.59, 815.56, 851.08, 925.62, 1015.72, 1092.33, 1106.35, 1134.64, 1161.58, 1177.05, 1223.03, 1250.85, 1269.21, 1372.89, 1393.61, 1414.83, 1427.00, 1453.03, 1538.35, 1566.63, 1735.33, 1966.88, 2085.17, 2279.30, 2330.47, 2864.69, 3486.30. HRMS m/z calculated for $[\text{C}_{83}\text{H}_{22}\text{O}_8\text{NH}_4]^+$: 1164.16529, found: 1164.16589. UV-Vis: $\lambda_{\text{max}}(\text{CHCl}_3)[\text{nm}] = 354$ (ϵ [$\text{M}^{-1}\text{cm}^{-1}$] 30800), 369 (29300), 403 (23600), 461 (27600), $\sim 540\text{inf}$, $\sim 660\text{inf}$ (1670).

[70]BTEG-2: Synthesis according to the general procedure for C₇₀ Bingel adducts: C₇₀ (0.421 g, 0.50 mmol, M2 (0.21 mL, should have been 0.21 g which would be 0.5 mmol), I₂ (0.067 g, 0.26 mmol) and DBU (0.16 mL, 1.1 mmol). Reaction time was 18 h. Eluent for column chromatography: 40% THF in toluene. [70]BTEG-2 was obtained as a black powder (180 mg, 30%). ¹H NMR (600 MHz, CDCl₃) δ 4.60 (q, J = 5.9, 3.7 Hz, 4H), 3.87 (t, J = 4.8 Hz, 4H), 3.74 – 3.69 (m, 4H), 3.69 – 3.63 (m, 9H), 3.59 – 3.53 (m, 4H), 3.38 (s, 5H). ¹³C NMR (151 MHz, CDCl₃) δ 163.76, 155.46, 151.71, 151.54, 151.08, 150.95, 149.71, 149.63, 149.48, 149.11, 148.94, 148.88, 148.85, 147.98, 147.89, 147.67, 147.38, 146.83, 146.31, 146.28, 145.25, 144.31, 144.21, 143.91, 143.24, 143.20, 142.66, 142.00, 141.21, 137.29, 133.92, 133.19, 131.30, 131.27, 131.18, 77.58, 77.37, 77.16, 72.33, 71.10, 71.07, 71.02, 69.10, 66.66, 59.45, 37.38. FT-IR (cm⁻¹): 670.96, 691.56, 725.45, 742.08, 707.26, 751.54, 762.38, 794.08, 842.93, 1020.80, 1083.42, 1223.39, 1268.38, 1426.45, 1538.24, 1562.62, 1740.91, 1965.57, 2102.09, 2219.78, 2277.74, 2308.19, 2330.64, 2862.47, 3485.83. HRMS m/z calculated for [C₈₇H₃₀O₁₀Na]⁺: 1257.17, found: 1257.17312. UV-Vis: λ_{max}(CHCl₃)[nm] = 355 (ε [M⁻¹cm⁻¹] 24800), 370 (23700), 404 (19100), 462 (22300), ~540*inf*, ~660*inf* (1590).

[70]BTrEG-2: Synthesis according to the general procedure for C₇₀ Bingel adducts: C₇₀ (0.500 g, 0.60 mmol, M3 (0.2883g, 0.6 mmol, I₂ (0.1571 g, 0.62 mmol) and DBU (0.2 mL, 1.3 mmol). Reaction time was 20 h. Eluent for column chromatography: 5% ethanol in toluene. [70]BTrEG-2 was obtained as a black powder (197 mg, 25%). ¹H NMR (600 MHz, CDCl₃) δ 4.62 – 4.56 (m, 4H), 3.86 (t, J = 4.8 Hz, 4H), 3.72 – 3.68 (m, 4H), 3.68 – 3.63 (m, 16H), 3.56 – 3.52 (m, 4H), 3.38 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 163.54, 155.23, 151.50, 151.48, 151.31, 150.86, 150.72, 149.48, 149.41, 149.26, 148.88, 148.71, 148.65, 148.62, 147.75, 147.66, 147.44, 147.15, 146.60, 146.09, 146.05, 145.02, 144.09, 143.98, 143.68, 143.02, 142.98, 142.43, 141.77, 140.98, 137.06, 133.69, 132.97, 131.07, 131.04, 130.95, 96.27, 77.37, 77.16, 76.95, 72.10, 70.86, 70.81, 70.77, 70.70, 68.87, 66.92, 66.44, 66.31, 59.22, 37.14. HRMS m/z calculated for [C₉₁H₃₈O₁₂Na]⁺: 1345.22555, found: 1345.22652. UV-Vis: λ_{max}(CHCl₃)[nm] = 355 (ε [M⁻¹cm⁻¹] 22000), 370 (21100), 405 (17000), 461 (19700), ~540*inf*, ~660*inf* (1380).

[70]BC10-2: Synthesis according to the general procedure for C₇₀ Bingel adducts: C₇₀ (0.4230 g, 0.50 mmol, M4 (0.1923g, 0.5 mmol, 0.12 mL), I₂ (0.1320 g, 0.52 mmol) and DBU (0.16 mL, 1.1 mmol). Reaction time was 3 days. First column silica; 20% hexane/toluene used. The first fractions containing a large percentage of unreacted C₇₀ were set aside, and the remaining combined residue was purified with a second column using 1:1 hexane/toluene as eluent. The fractions were individually checked by HPLC for purity before combining. The procedure was repeated until

enough pure [70]BC10-2 was obtained as a black powder (272 mg, 44%). ^1H NMR (600 MHz, CDCl_3) δ 4.44 (td, $J = 6.6, 1.6$ Hz, 4H). ^1H NMR (600 MHz, CDCl_3) δ 4.44 (td, $J = 6.6, 1.6$ Hz, 4H), 1.86 – 1.79 (m, 4H), 1.51 – 1.44 (m, 4H), 1.36 (p, $J = 6.7$ Hz, 4H), 1.27 (dhept, $J = 18.0, 5.8$ Hz, 22H), 0.88 (t, $J = 7.0$ Hz, 6H). ^{13}C NMR (151 MHz, CDCl_3) δ 163.73, 155.24, 151.52, 151.50, 151.31, 150.86, 150.72, 149.48, 149.40, 149.25, 148.85, 148.71, 148.65, 148.62, 147.79, 147.67, 147.44, 147.14, 146.60, 146.07, 146.05, 145.00, 144.09, 143.98, 143.67, 143.11, 142.97, 142.35, 141.80, 140.90, 137.14, 133.71, 132.96, 131.07, 131.03, 130.95, 77.37, 77.16, 76.95, 67.71, 67.06, 66.39, 37.51, 32.06, 29.81, 29.75, 29.52, 29.42, 28.74, 26.18, 22.87, 14.31. HRMS m/z calculated for $[\text{C}_{93}\text{H}_{42}\text{O}_4\text{H}]^+$: 1223.31613, found: 1223.3175. UV-Vis: $\lambda_{\text{max}}(\text{CHCl}_3)[\text{nm}] = 354$ (ϵ [$\text{M}^{-1}\text{cm}^{-1}$] 26900), 371 (25800), 403 (20700), 463 (24100), $\sim 540\text{inf}$, $\sim 660\text{inf}$ (1700).

2 NMR spectra

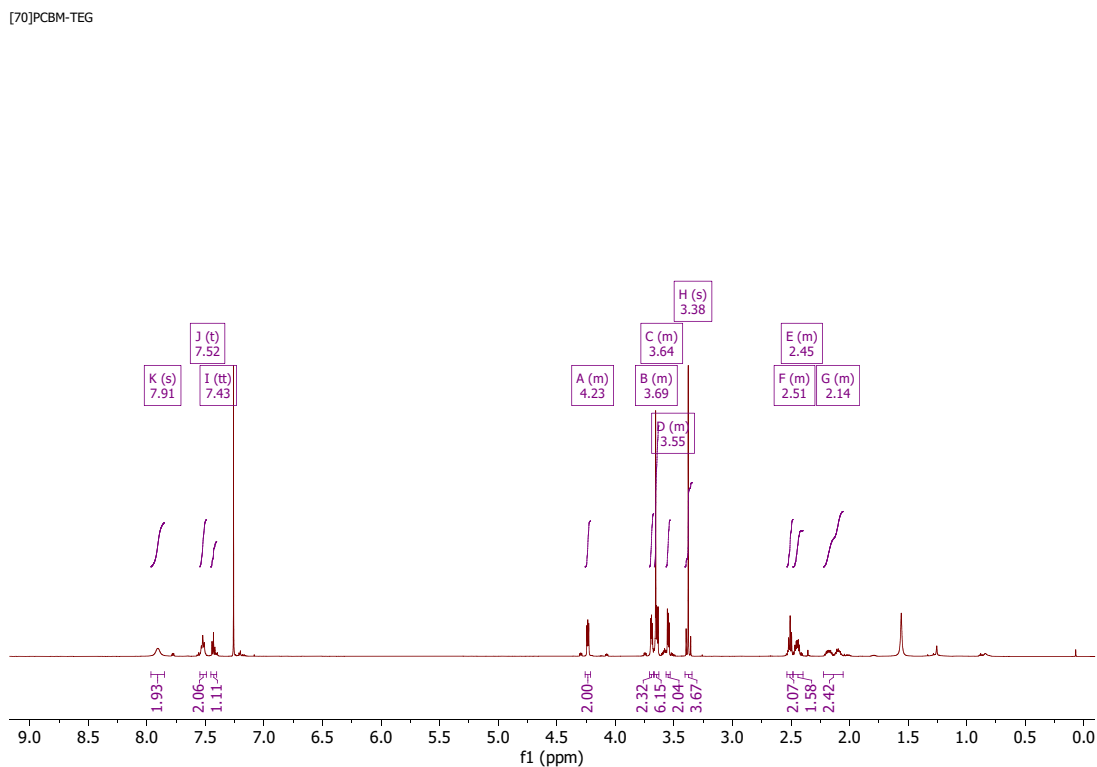


Figure S3: ^1H NMR spectrum for [70]PCBM-TEG

[70]BDEG-2

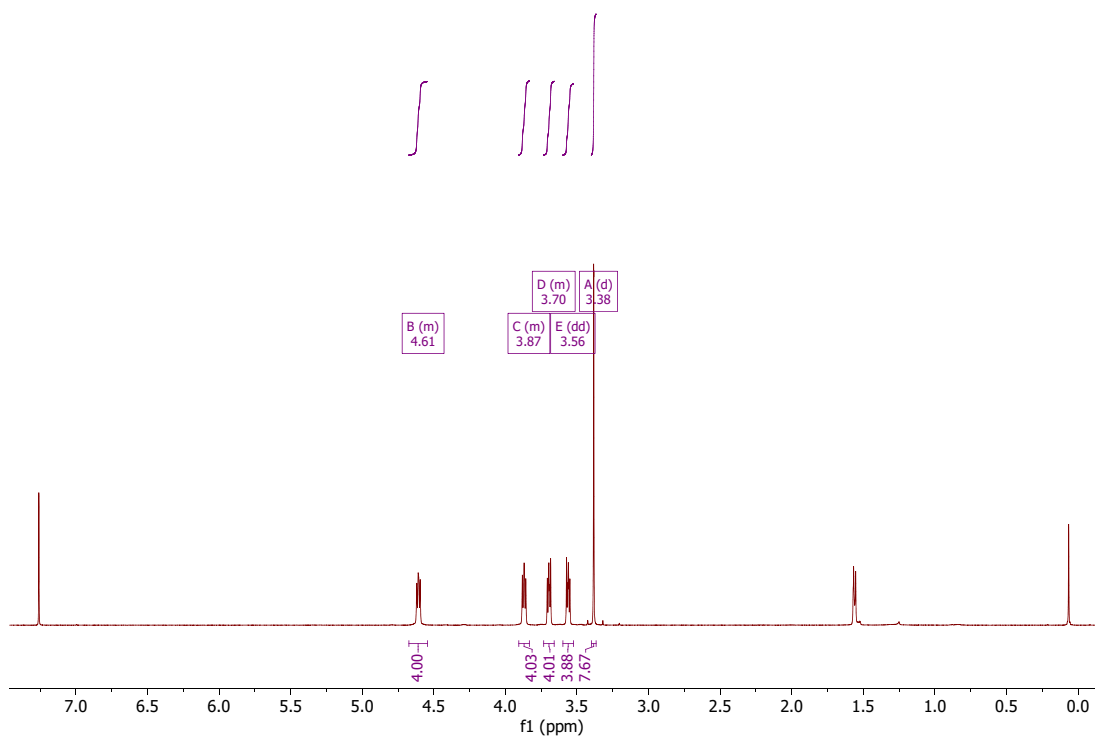


Figure S4: ¹H NMR spectrum of [70]BDEG-2

[70]BTEG-2

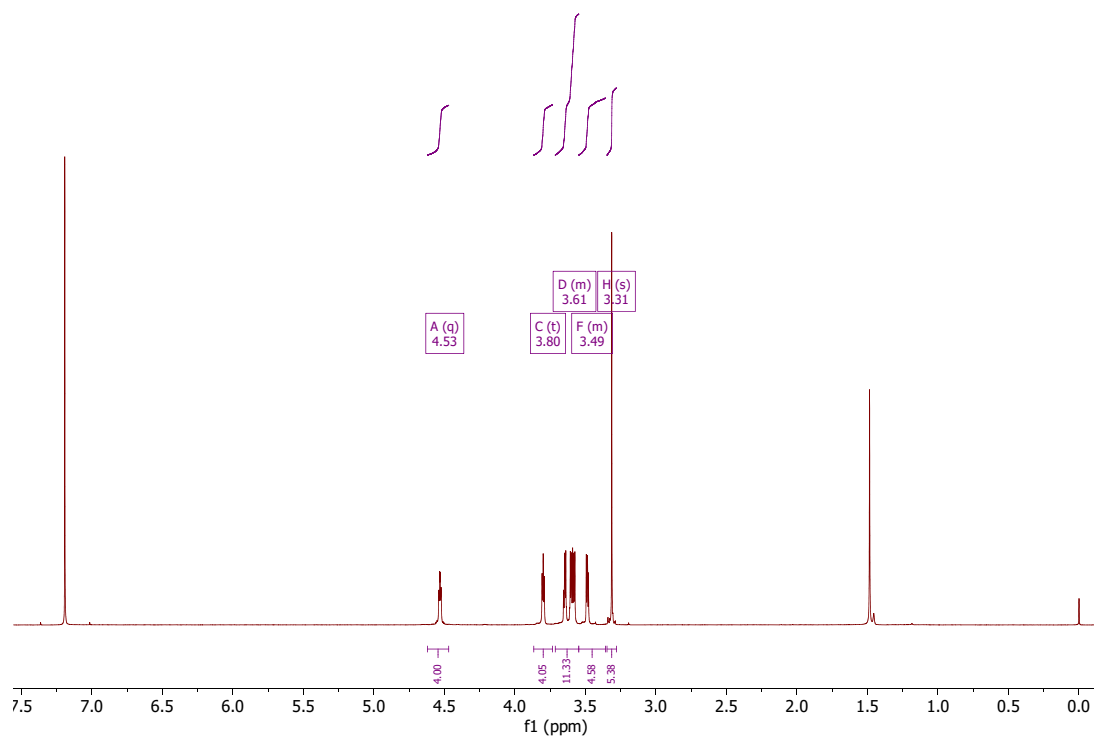


Figure S5: ¹H NMR spectrum of [70]BTEG-2

[70]BTrEG-2

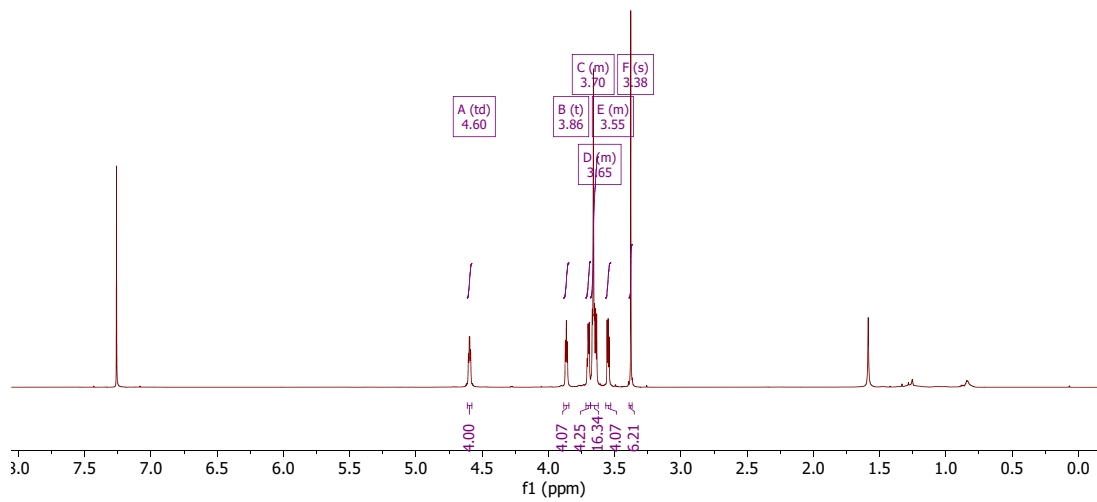


Figure S6: ^1H NMR spectrum of [70]BTrEG-2

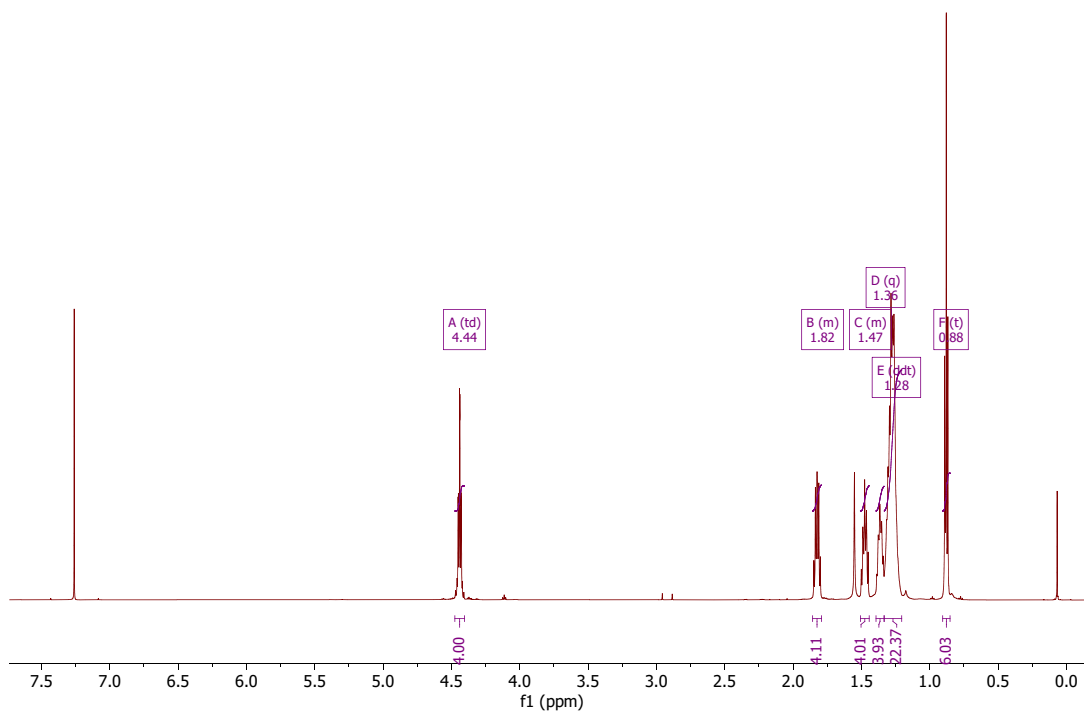


Figure S7: ¹H NMR spectrum of [70]BC10-2

3 Neat material properties

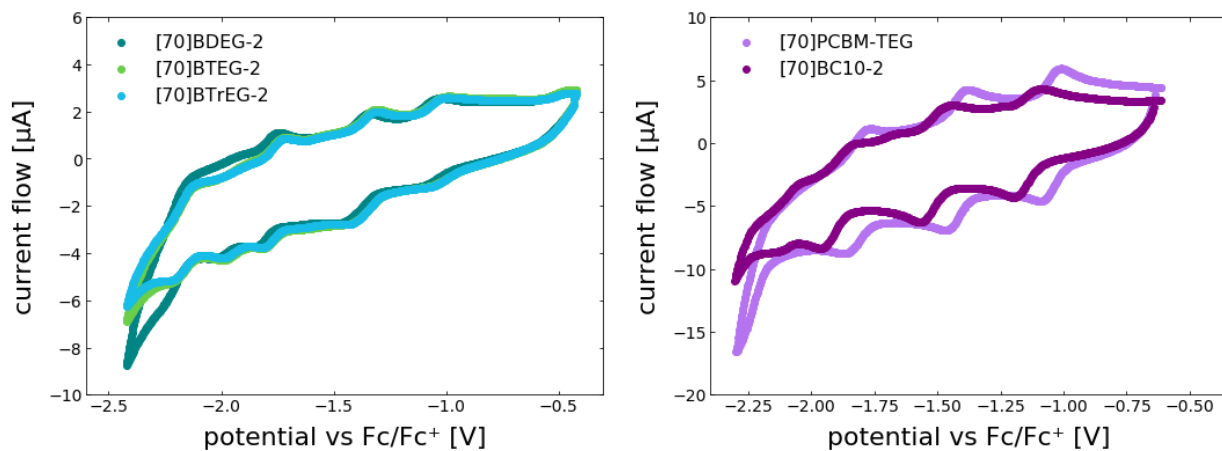


Figure S8: Cyclic voltamograms of the new C₇₀ derivatives in degassed 4:1 DCM/ODCB solutions containing TBAPF₆ as the electrolyte in 0.1M concentration.

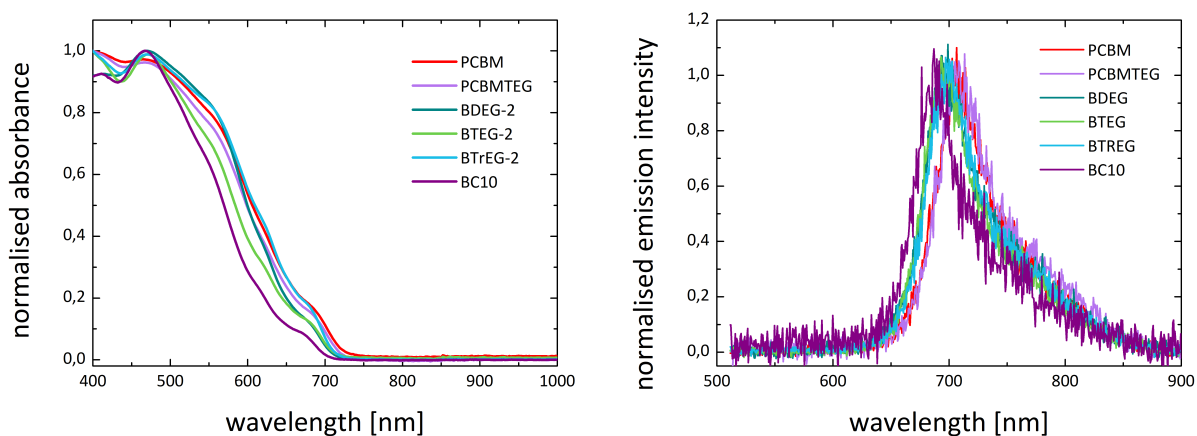


Figure S9: UV-Vis spectra (left) and steady state PL spectra (right) of the neat C₇₀ derivatives as films on glass slides. The excitation wavelength was 550 nm

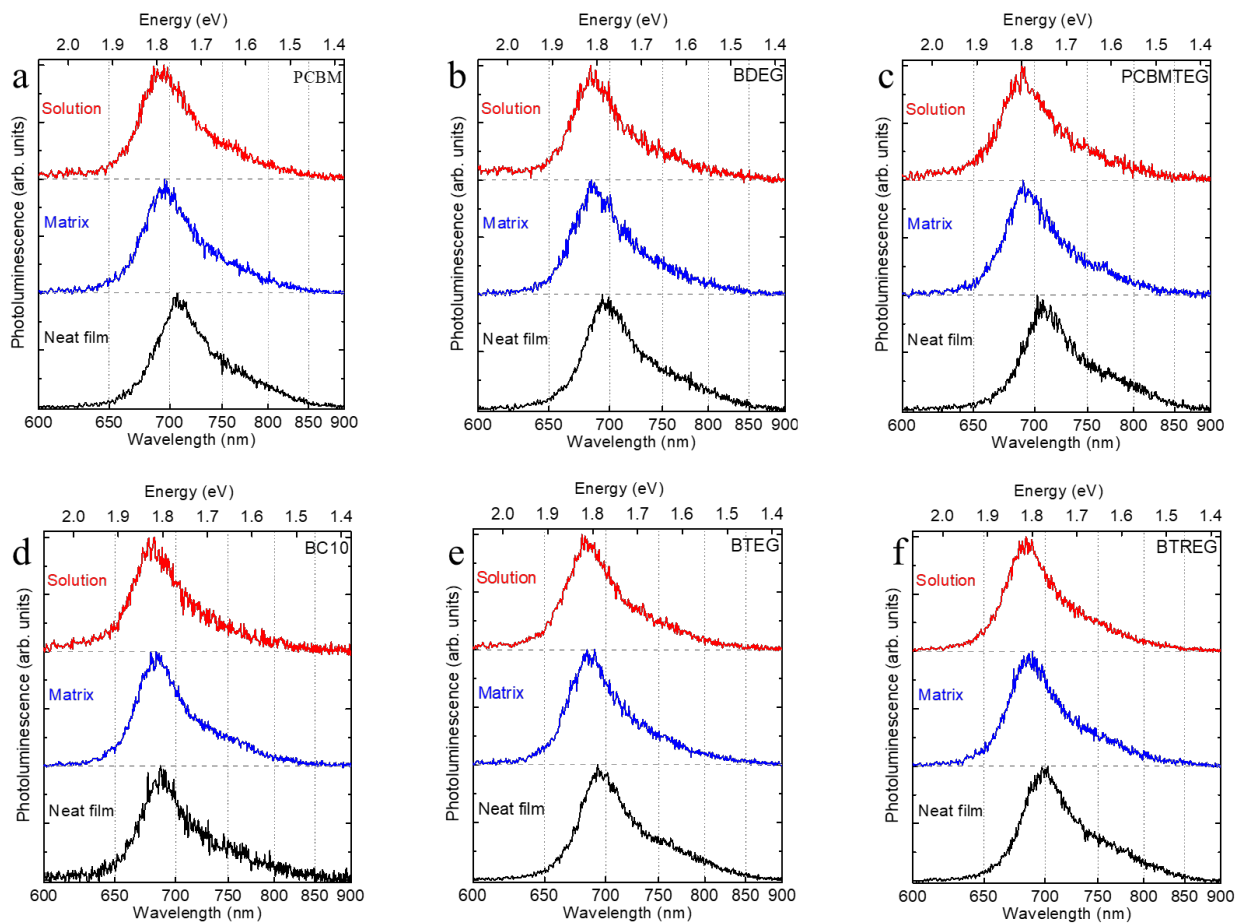


Figure S10: PL spectra of the fullerenes in CF solutions (red), PMMA matrices (blue) and neat films (black).

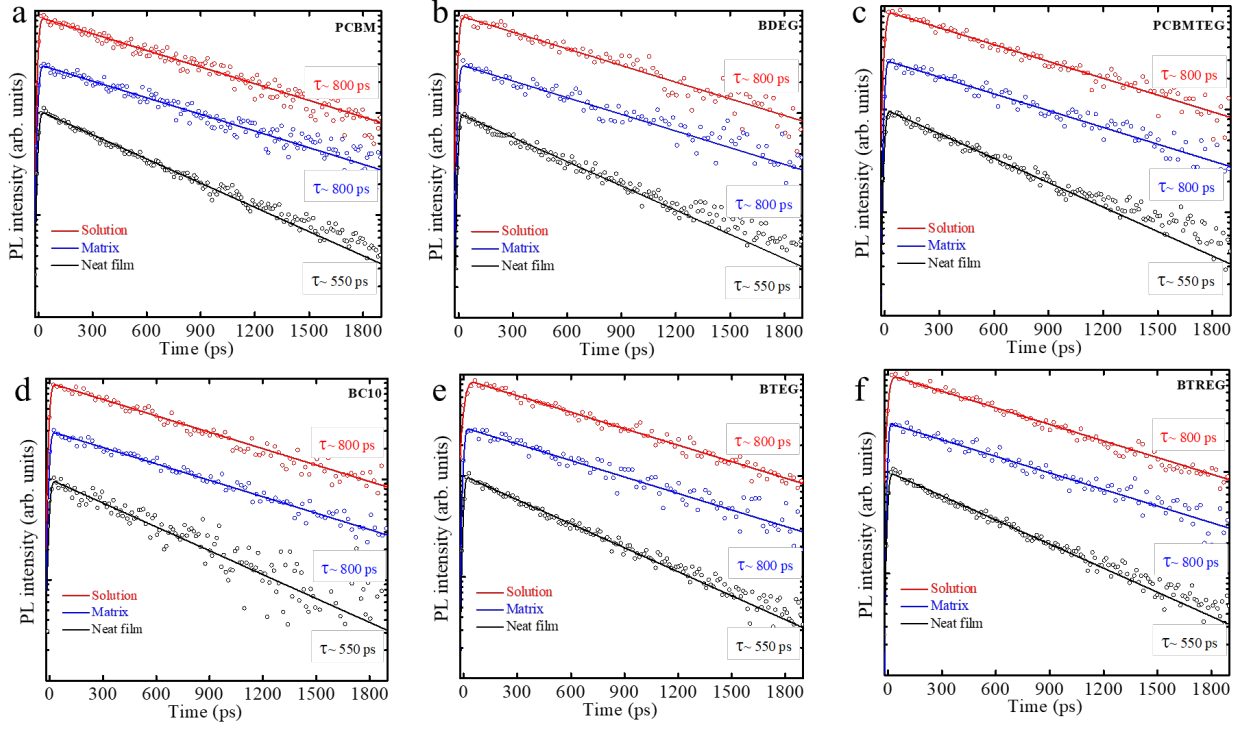


Figure S11: Logarithmic plots of the experimental PL transients of CF solutions (red), PMMA matrices (blue) and neat films (black) and the respective fitting (solid lines) convoluted with a Gaussian apparatus function of 10 ps. Each PL transient is re-scaled by a factor of 3 with respect to the previous for better visibility.

3.1 Average distance between excitons

The number of excitons per unit area (i.e., the exciton density) was calculated as:

$$n_e = \left(\frac{P_{avg}}{f_{rep}} \right) \left(\frac{\lambda_{exc}}{hc} \right) (1 - 10^{-OD_{\lambda_{exc}}}) \left(\frac{1}{\pi r_{focal}^2} \right) \quad (S1)$$

where P_{avg} is the average excitation power, f_{rep} is the repetition rate of laser pulses, λ_{exc} is the excitation wavelength, h is Planck's constant, c is the speed of light, $OD_{\lambda_{exc}}$ is the optical density at the excitation wavelength and r_{focal} is the radius of the excitation spot. The average distance between excitons (d) can be estimated as:

$$d = \frac{1}{\sqrt{n_e}} \quad (S2)$$

Parameter	Description	Excitation @ 550 nm	Excitation @ 405 nm
P_{avg}	average power	10-200 μ W	30-340 μ W
f_{rep}	pulse repetition rate	76 MHz	2 MHz
$OD_{\lambda_{exc}}$	optical density at λ_{exc}	0.22	\sim 0.3
r_{focal}	radius of excitation spot	30 μ m	110 μ m
n_e	exciton density	5×10^{13} - 1×10^{15} cm^{-2}	4×10^{14} - 5×10^{15} cm^{-2}
d	average distance between excitons	140 - 30 nm	50 - 14 nm

Table S1: Parameters used to calculate the average distance between excitons at varying excitation power in neat films

4 Blended films

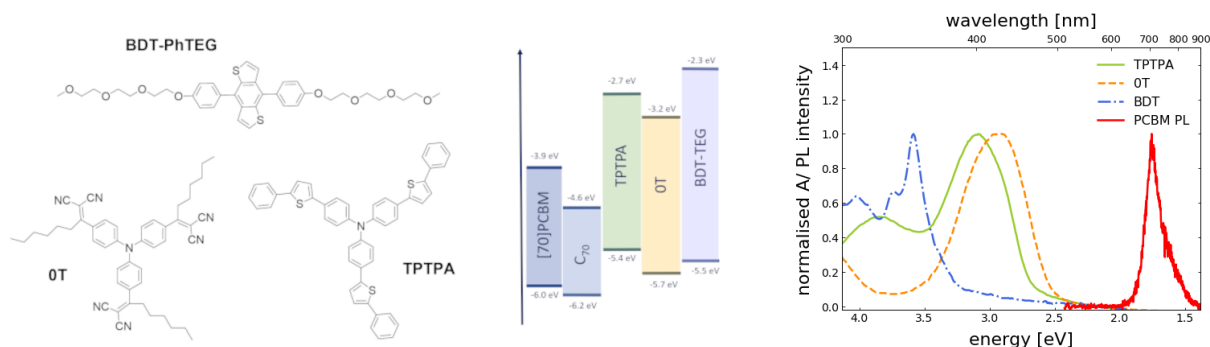


Figure S12: Chemical structures of the materials used as quenchers in the PL quenching experiments (left); energy level diagram of the quenchers used for the exciton diffusion length measurements (centre). The values for [70]PCBM and C₇₀ and TPTPA are taken from the literature,³ whereas the values for OT and BDT-PhTEG were estimated very roughly from cyclic voltammetry and the optical HOMO-LUMO gap; and the absorption of the three quenchers overlaid with the fluorescence spectrum [70]PCBM (right) shows no overlap between the quencher absorption and the host emission for all three cases.

4.1 Monte-Carlo Simulations

A detailed description of the Monte-Carlo simulations can be found in a previous paper.⁴ The exciton lifetime in the neat film, the hopping distance and the quencher content were used as input parameters. The hopping distance was estimated by calculating the average size of the molecules over three dimensions with (Equation S3):

$$S = \sqrt[3]{\frac{M_m}{\rho N_A}} \quad (\text{S3})$$

where S ($\sim 1.1\text{nm}$) is the size of the molecule, ρ is the density (1.5 gcm^{-3}), M_m is the molar mass and N_A is Avogadro's constant.

The input parameters used are given in Table S1.

Parameter	Description	Value
τ	lifetime	550 ps
S	hopping distance	~ 1.1 nm
QF	quencher fraction (mols)	0-0.1
σ	energetic disorder	~ 25 meV
t	hopping time	~ 2 ps

Table S2: Input parameters for the Monte-Carlo simulations used to estimate the L_D for [70]PCBM, PCBM-TEG and BDEG

The exciton diffusion length (~ 10 nm) was taken as the mean value of the exciton displacement statistics obtained from the MC-simulations. The exciton diffusion coefficient of was determined using the differential form of Einstein-Smoluchowski relation:

$$D(t) = \frac{\partial \langle l^2(t) \rangle}{6\partial t} \quad (S4)$$

where $\langle l^2 \rangle$ is the average square of the exciton displacement and t is the diffusion time.

4.2 UV-Vis spectra

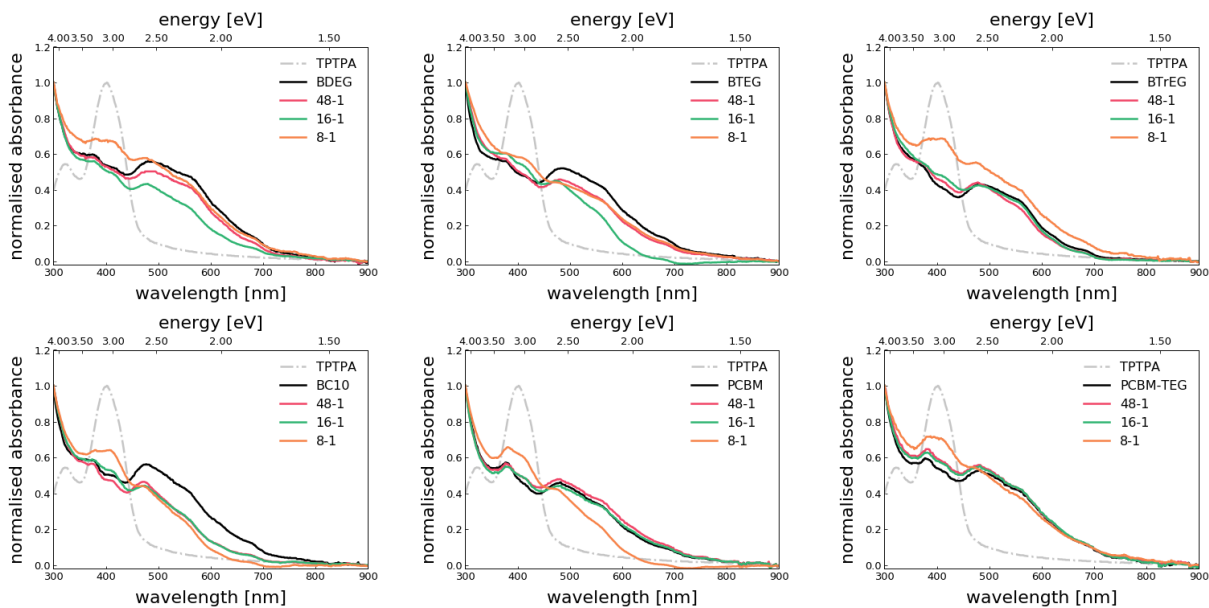


Figure S13: UV-Vis spectra of the C₇₀ derivatives in blended films with TPTPA. The ratios are weight ratios of fullerene:TPTPA and the spectra are normalised to the maximum absorbance

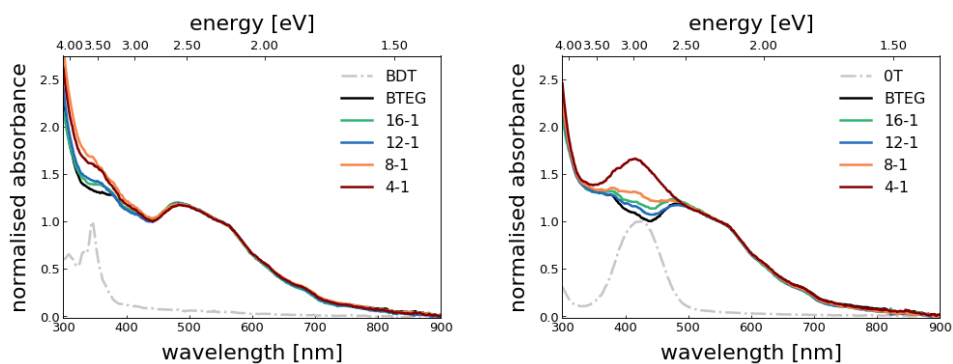


Figure S14: UV-Vis spectra of blended films of BTEG with different weight ratios of BDT-TEG (left) and OT (right), normalised at 550 nm.

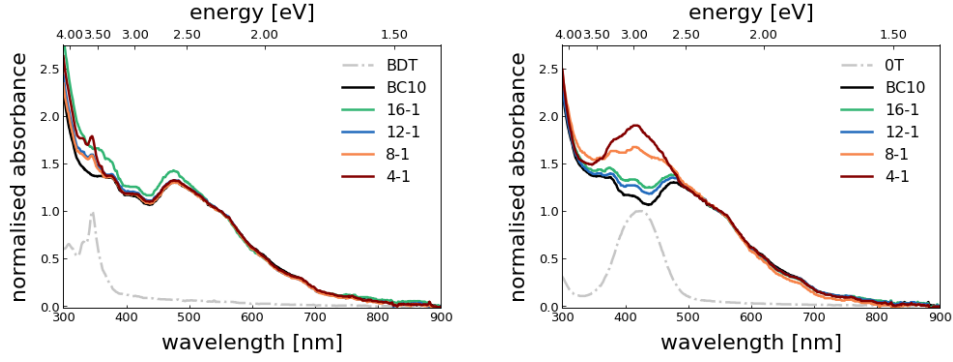


Figure S15: UV-Vis spectra of blended films of BC10 with different weight ratios of BDT-TEG (left) and OT (right), normalised at 550 nm.

4.3 Time-resolved PL

The lifetime of the fullerene PL was determined by fitting the following equation to the data:

$$F(t) = \frac{e^{-\frac{t^2}{2\sigma^2}}}{\sigma\sqrt{2\pi}} \otimes Ae^{-\frac{t}{\tau}} \quad (\text{S5})$$

where $\sigma=10$ ps, the standard deviation of the apparatus function, A is the amplitude and τ is the excited state lifetime.

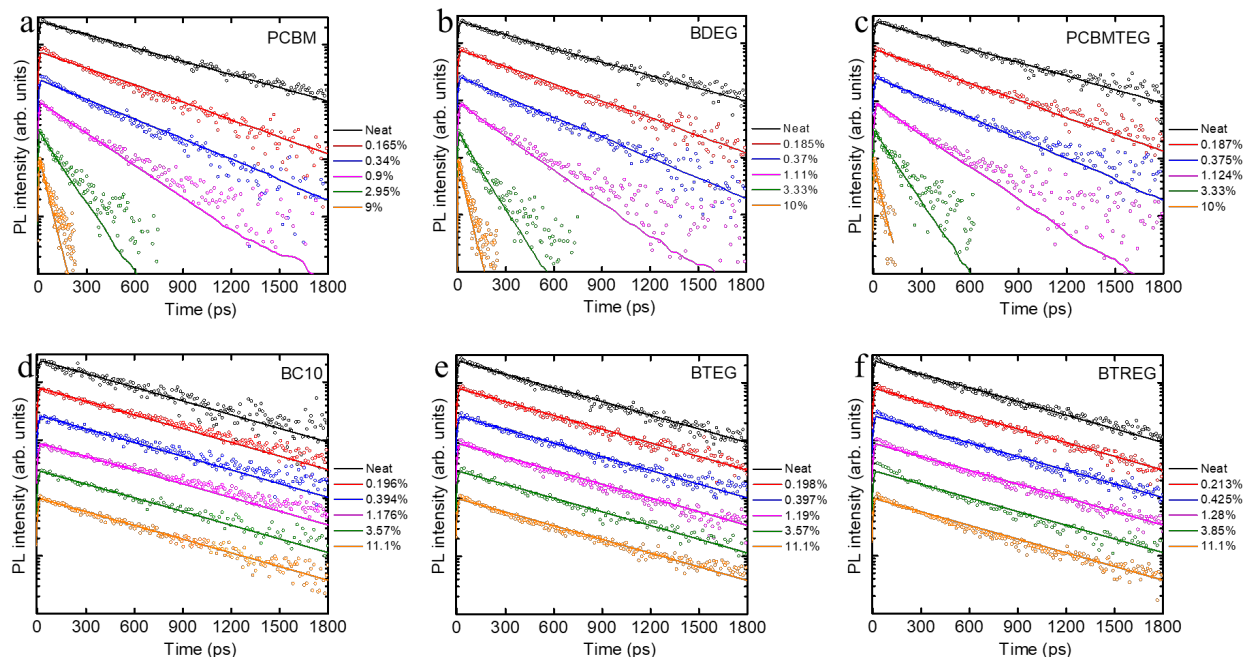


Figure S16: PL decay curves of the C_{70} derivative films with various ratios of TPTPA (given as mol%). $\lambda_{exc} = 550$ nm in all cases and the PL transients are normalised and arbitrarily offset along the y-axis for better visibility. In (a-c), the fitted line denotes the results of decay curves obtained using the Monte-Carlo simulations (details in SI), whereas for (d-f) the line shows the fitting for mono-exponential decay with $\tau = 550$ ps

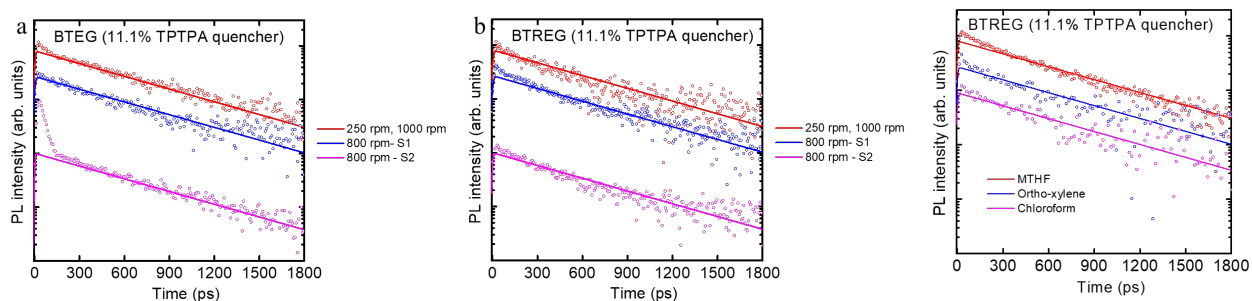


Figure S17: PL transients for BTEG:TPTPA and BTrEG:TPTPA films spin-cast using different conditions, and BTrEG:TPTPA films spin-cast from different solvents. $\lambda_{exc} = 550$ nm. The solid lines show the result of fitting a mono-exponential decay function with $\tau = 550$ ps.

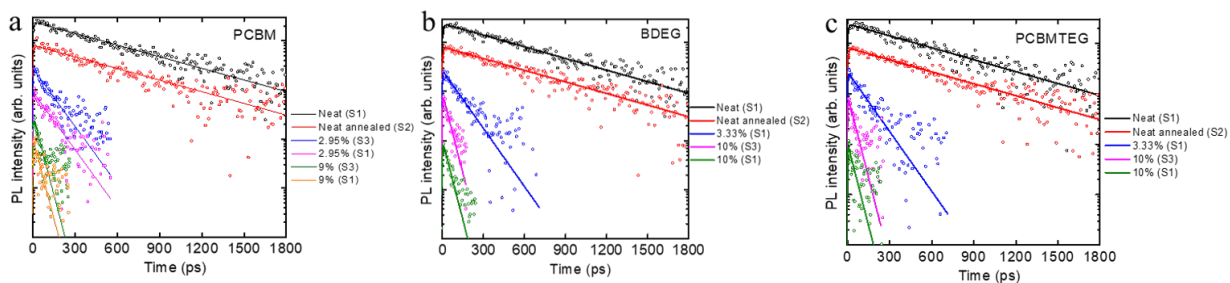


Figure S18: Time-resolved PL decays of blended films containing PCBM, PCBM-TEG, BDEG and TPTPA, spin-cast with different spin conditions, showing that the PL dynamics is independent of the spincoating program in the case of the 'well-behaved' fullerene derivatives. $\lambda_{exc} = 550$ nm. The solid lines show the results of the MC-model fitted to the data

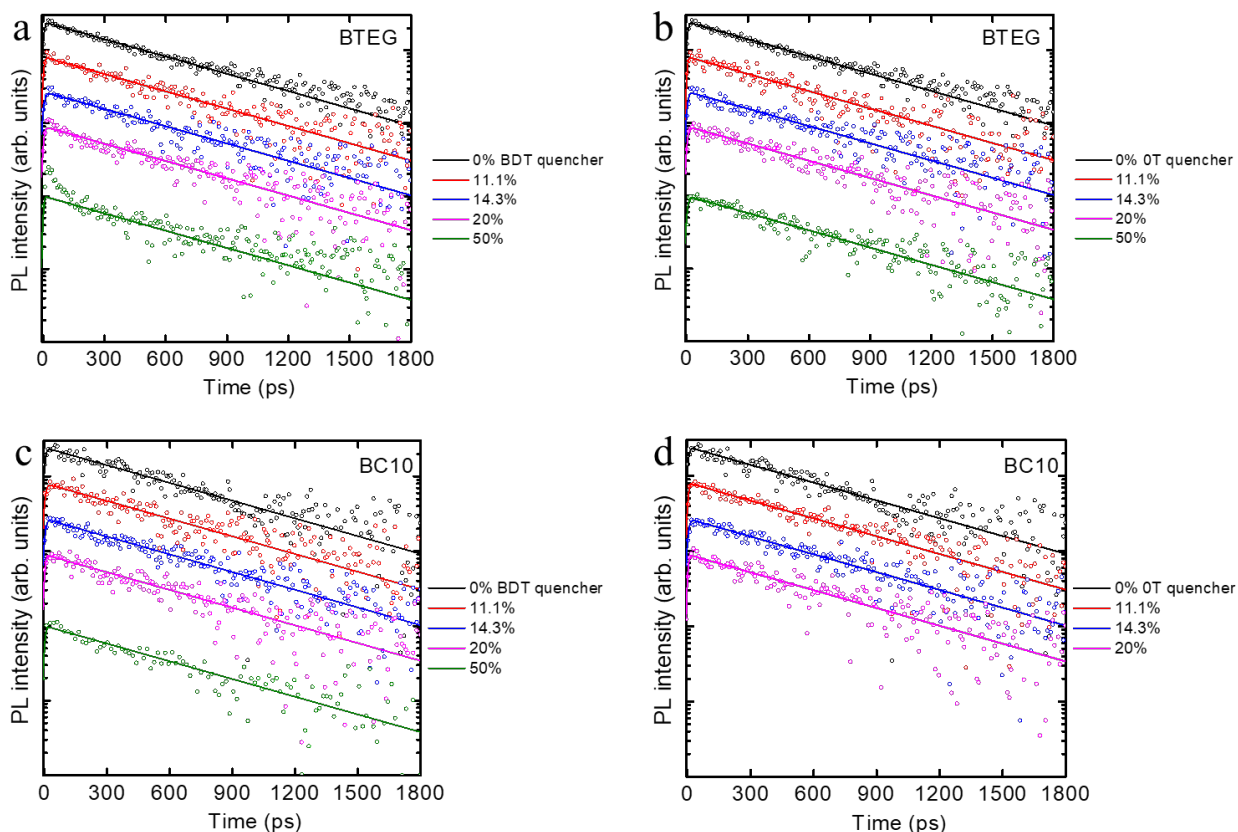


Figure S19: PL decay curves of [70]BTEG-2 (top) and [70]BC10-2 (bottom) films with BDT-PhTEG (left) and OT (right) as alternative quenchers. The ratio of fullerene: quencher is given as mol%, and $\lambda_{exc} = 550$ nm in all cases. The PL transients are normalised and arbitrarily offset along the y-axis for better visibility. The solid lines denote the mono-exponential fit with $\tau = 550$ ps.

5 AFM images

5.1 Blends with TPTPA as quencher

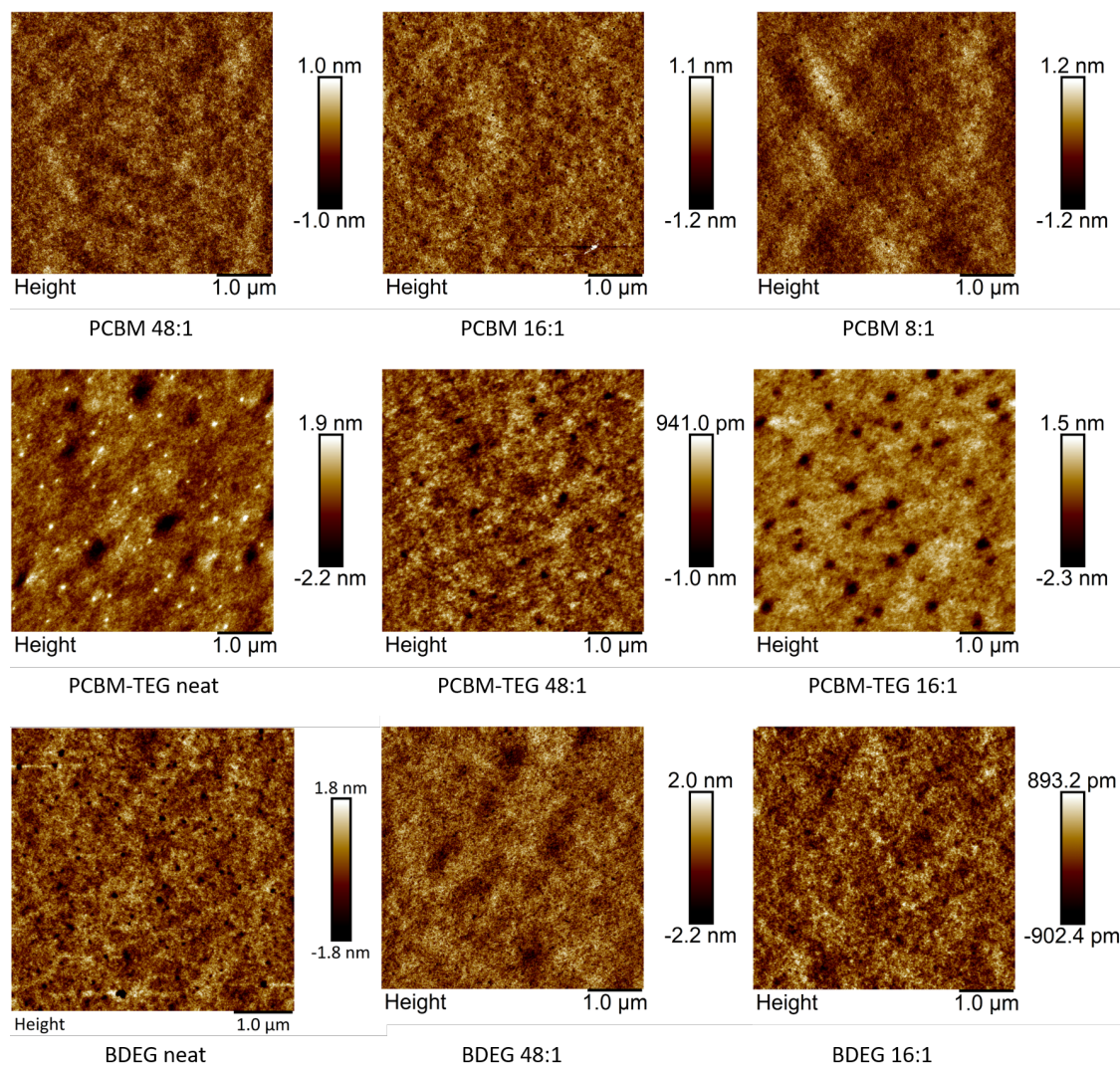


Figure S20: AFM images of [70]PCBM, [70]PCBM-TEG and [70]BDEG-2 films containing an increasing amount (left to right) of TPTPA. The fullerene:TPTPA weight ratios are given.

5.2 Blends with BDT-PhTEG and OT

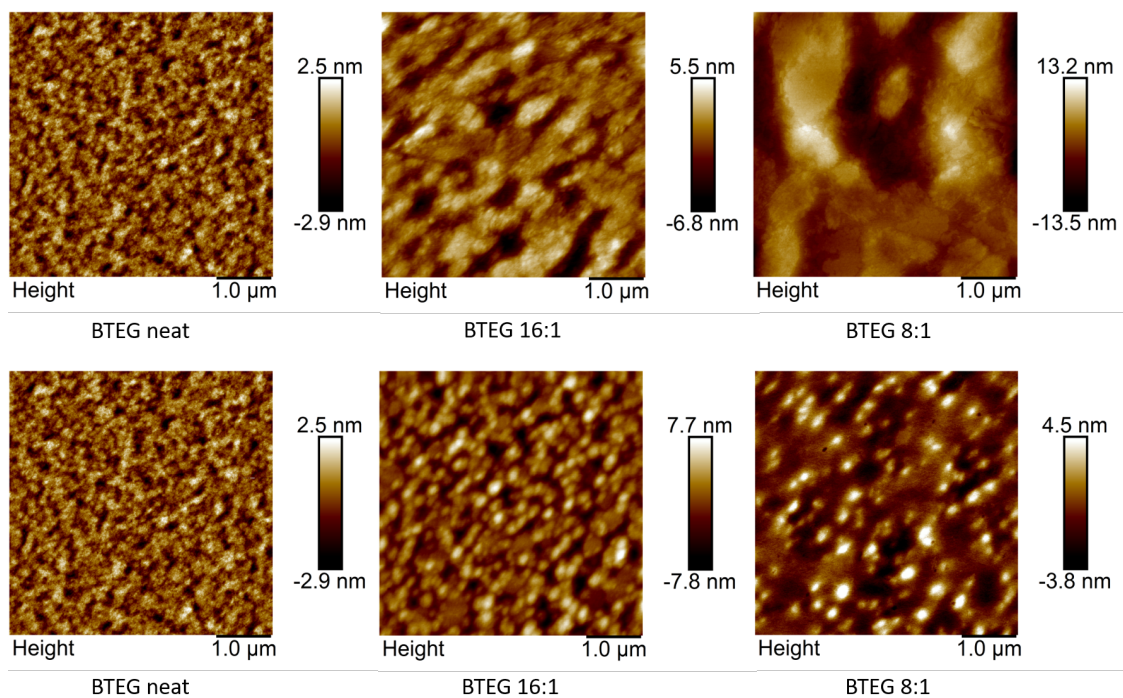


Figure S21: AFM images of [70]BTEG-2 films containing various weight ratios of BDT-PhTEG (top) and OT (bottom).

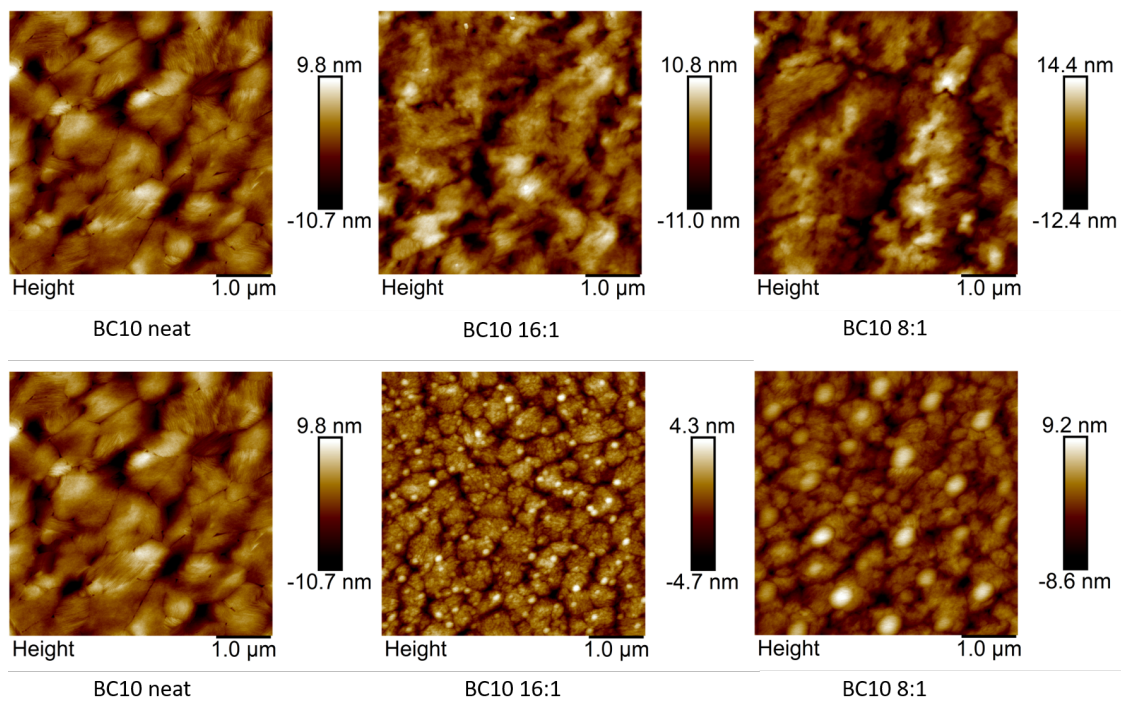


Figure S22: AFM images of [70]BC10-2 films containing various weight ratios of BDT-PhTEG (top) and OT (bottom).

6 Dielectric properties

6.1 Impedance spectroscopy

Parallel plate capacitors were fabricated with the device structure glass/ITO/PEDOT:PSS (~50 nm)/fullerene-derivative/aluminium (~100 nm) on pre-patterned ITO substrates with four active areas per sample of varying dimensions (9 mm², 16 mm², 36 mm² and 100 mm²). Impedance measurements were carried out in the frequency range 10-10⁶ Hz with an AC drive voltage of 10-20 mV and no applied DC bias. The capacitance was obtained by equivalent circuit fitting and ϵ_r was calculated using the parallel plate capacitor equation for each individual device:

$$\epsilon_r = \frac{Cd}{\epsilon_0 A} \quad (\text{S6})$$

where ϵ_0 is the permittivity of vacuum [Fm⁻¹], C is the measured capacitance [F], d is the thickness [m] and A is the device area [m²]. 8-18 devices of various sizes and thicknesses were measured for each material and the ϵ_r was the average value obtained for all devices.

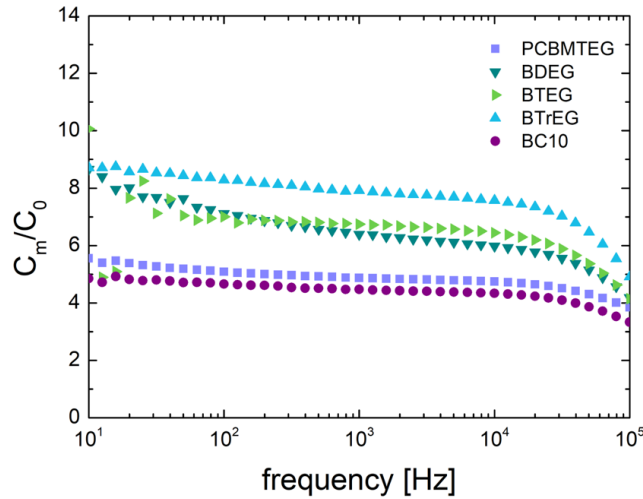


Figure S23: The dielectric response across frequency for one representative device of each C₇₀ derivative, measured by impedance spectroscopy.

6.2 Ellipsometry

Samples for ellipsometry were prepared by spincoating neat films of the fullerene derivative from CF solutions onto cleaned glass substrates. The back side of the substrate was covered with black tape to prevent reflections from the back interface and simplify the fitting procedure. Each sample was measured in two different spots at three incident angles (58, 60 and 62°). The blank substrate was also measured and the optical constants modelled using the Cauchy model provided by the WVASE software and used as the first layer for all subsequent fittings. For each sample, the thickness of the film was first obtained by applying the Cauchy model to the spectral range 800-1800 nm where the fullerene absorption was minimal.

A general oscillator model was then constructed using the data from the [70]PCBM samples. First, the refractive index (n) and extinction coefficient (k) values were roughly approximated by carrying out a 'point by point' fit of the full spectral range (400-1800 nm) using the Cauchy model with the other model parameters and the thickness fixed. The general oscillator model was built using WVASE by fitting a series of Gaussian oscillator functions to the extinction coefficients obtained from the Cauchy estimate. The Gaussian functions represent the electronic transitions in the material. The number of Gaussian functions and the energy at which they were placed was decided by looking at the local maxima in the UV-Vis absorption spectra and at the polarisation variations in the $\tan(\psi)$ spectrum. After a good fit was obtained for k , the n values were calculated by WVASE using the Kramers-Kronig relations.

The model built for [70]PCBM was used for both the methano-fullerenes and was tweaked for the Bingel adducts to accommodate the small differences in the absorption spectra of the two groups of fullerenes. The final mean squared error for the fit result lay in the range of 6-12 for all samples measured. The approach and final results were similar to the work of Aboura *et al.*⁵

Function	PCBM model			BDEG-2 model		
	Energy [eV]	Amp. [a.u]	Br. [eV]	Energy [eV]	Amp. [a.u]	Br. [eV]
Gaussian 1	3.83	4.43	0.93	3.83	4.43	0.83
Gaussian 2	2.95	1.17	0.62	2.95	1.32	0.56
Gaussian 3	2.52	1.16	0.41	2.54	1.26	0.39
Gaussian 4	2.20	0.91	0.37	2.22	0.89	0.35
Gaussian 5	1.88	0.13	0.21	1.93	0.11	0.20

Table S3: Parameters for the general oscillator model representing the extinction coefficient (k) spectrum/ imaginary part of the dielectric function for the methano-fullerene [70]PCBM and the Bingel adduct [70]BDEG-2.

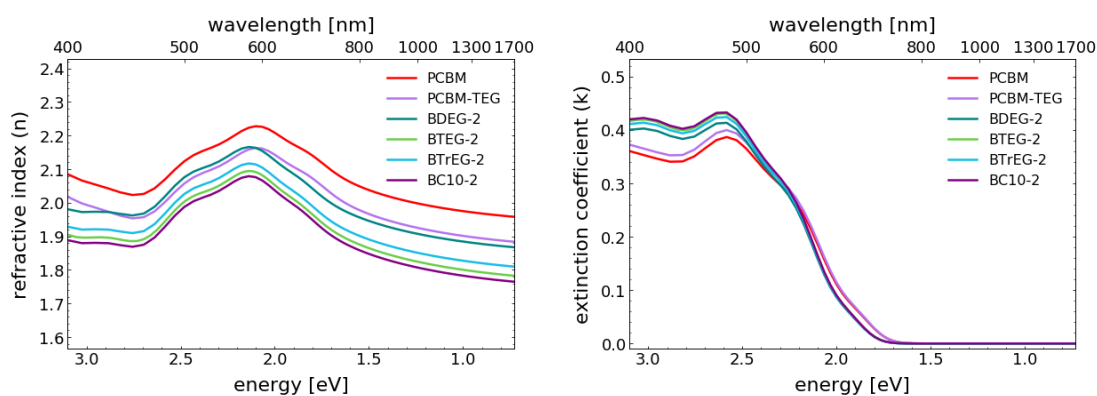


Figure S24: The obtained refractive index (left) and extinction coefficient (right) for the C_{70} derivatives studied in this work. Two samples were measured per material and the graph depicts the average values obtained using the general oscillator model described above.

7 Differential scanning calorimetry

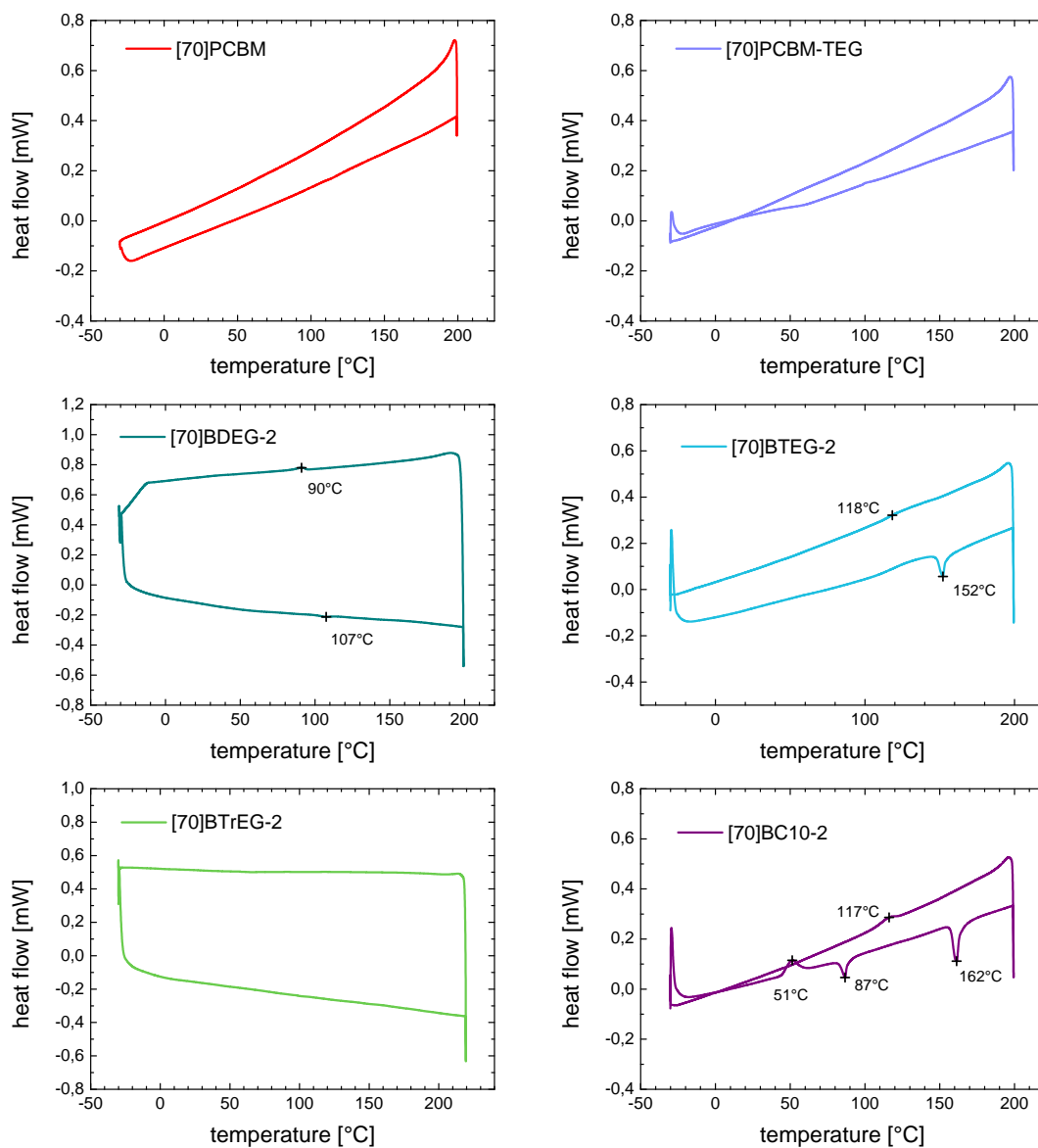


Figure S25: DSC scans of the C_{70} derivatives. The samples consisted of 1-3 mg of fullerene powder placed in a sealed Tzero aluminium pan. 2-3 heating/cooling cycles were measured, and the second scan only is plotted. The samples were heated at a rate of 10 °C/min and cooled at 5 °C/min except BDEG-2 where the cooling rate was 15 °C/min. The endo and exothermic transitions corresponding to melting and crystallisation processes respectively, are labelled with a black cross.

References

- (1) Douvogianni, E.; Qiu, X.; Qiu, L.; Jahani, F.; Kooistra, F. B.; Hummelen, J. C.; Chiechi, R. C. *Chemistry of Materials* **2018**, *30*, 5527–5533.
- (2) Rousseva, S.; den Besten, H.; van Kooij, F. S.; Doting, E. L.; Doumon, N. Y.; Douvogianni, E.; Koster, L. J. A.; Hummelen, J. C. *The Journal of Physical Chemistry C* **2020**, *124*, 8633–8638.
- (3) Kozlov, O. V.; de Haan, F.; Kerner, R. A.; Rand, B. P.; Cheyns, D.; Pshenichnikov, M. S. *Physical Review Letters* **2016**, *116*, 057402.
- (4) Raul, B. A. L.; Luponosov, Y. N.; Yang, W.; Surin, N. M.; Douhéret, O.; Min, J.; Jansen, T. L. C.; Ponomarenko, S. A.; Pshenichnikov, M. S. *Scientific Reports* **2020**, *10*, DOI: 10.1038/s41598-020-78197-2.
- (5) Aboura, F. B.; Duché, D.; Simon, J.; Escoubas, L. *Chemical Physics* **2015**, *450-451*, 102–108.