

Supplementary Data

Improving the compatibility of Fullerene Acceptors with Fluorene-Containing Donor-Polymers in Organic Photovoltaic Devices

Jan-Carlos Kuhlmann,^a Paul de Bruyn,^{b,c} Ricardo K. M. Bouwer,^{a,c} Auke Meetsma,^b Paul W. M. Blom^b and Jan C. Hummelen^{*a,b}

^a Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands. Fax: +31 50 363 8751; Tel: +31 50 363 5553; E-mail: j.c.hummelen@rug.nl

^b Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.

^c Dutch Polymer Institute, P.O. Box 902, 5600 AX Eindhoven, The Netherlands

Experimental procedure for fabrication of solar cells

PF10TBT:fullerene solutions were prepared by dissolving 3 mg/mL PF10TBT and 12 mg/mL fullerene in chlorobenzene at 90 °C. Devices were prepared on ITO coated glass substrates. The substrates were scrubbed with soap, put in a flow bath with deionized water, sonicated in acetone, rinsed with deionized water, sonicated in 2-isopropanol, spun dry, dried at 140 °C in an oven and received UV-ozone treatment for 20 minutes. A 50 nm layer of PEDOT:PSS (CLEVIOS P VP AI 4083) was applied as anode buffer layer. The active layers were spin cast at elevated temperature (90 °C) on top of the PEDOT:PSS layer. One nm of lithium fluoride and 100 nm of aluminium were used as cathode for all devices. Multiple sets of devices were prepared. One with 1:4 weight ratios of polymer and fullerene and one with altered ratios to take into account the differences in molecular weights of the fullerenes. Across both sets the open-circuit voltages are consistently higher for the FCBM devices in comparison to the PCBM devices. Figure 1 illustrates this fact. Illumination was done with a Steuernagel Solar Constant 1200 metal halide lamp. The lamp was calibrated with a silicon reference device and corrected for spectral mismatch with the AM1.5G spectrum by means of the spectral response. Electrical characterization was done with a Keithley Source Meter 2400. Spectral response measurements were done with a custom setup using a quartz tungsten halogen source, calibrated with a silicon photodiode. Halogen lights were used to provide white bias lighting on the cells. IPCE measurements for devices with equal weight ratios are shown in figure 2. Data points represent an average over four devices on one substrate ranging from 9 mm² to 1 cm². The error bars represent the typical spread in spectral response over these four devices.

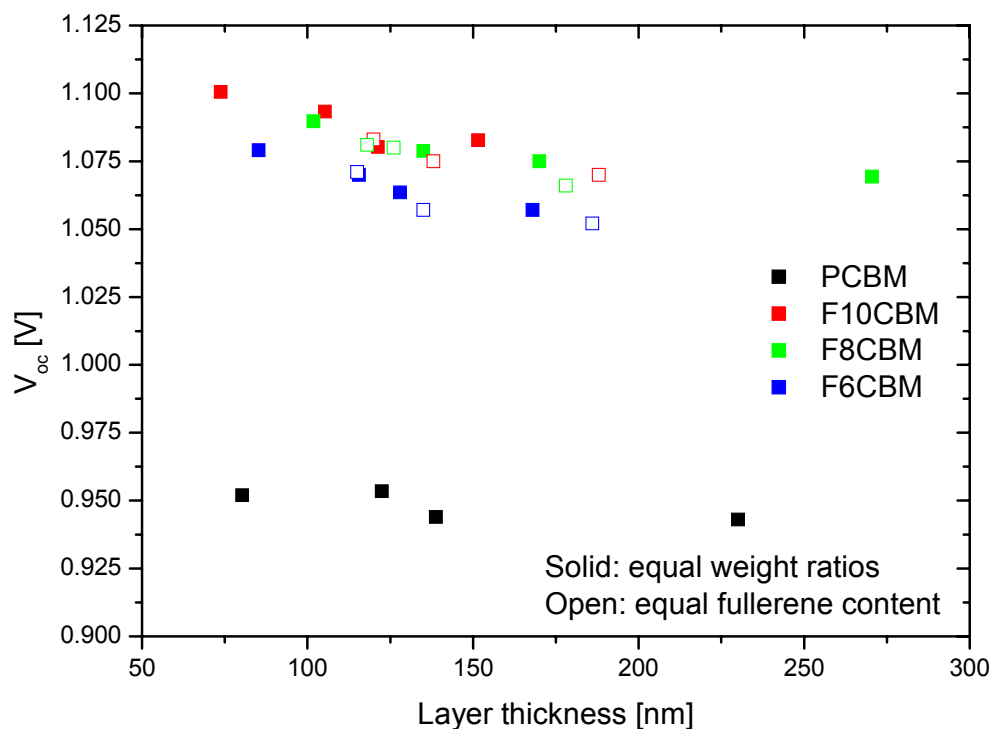


Figure S1. Open-circuit voltages of polymer:fullerene devices for devices with equal weight ratios of polymer and fullerene (solid symbols) and devices with equal molar fullerene fraction in the blends (open symbols).

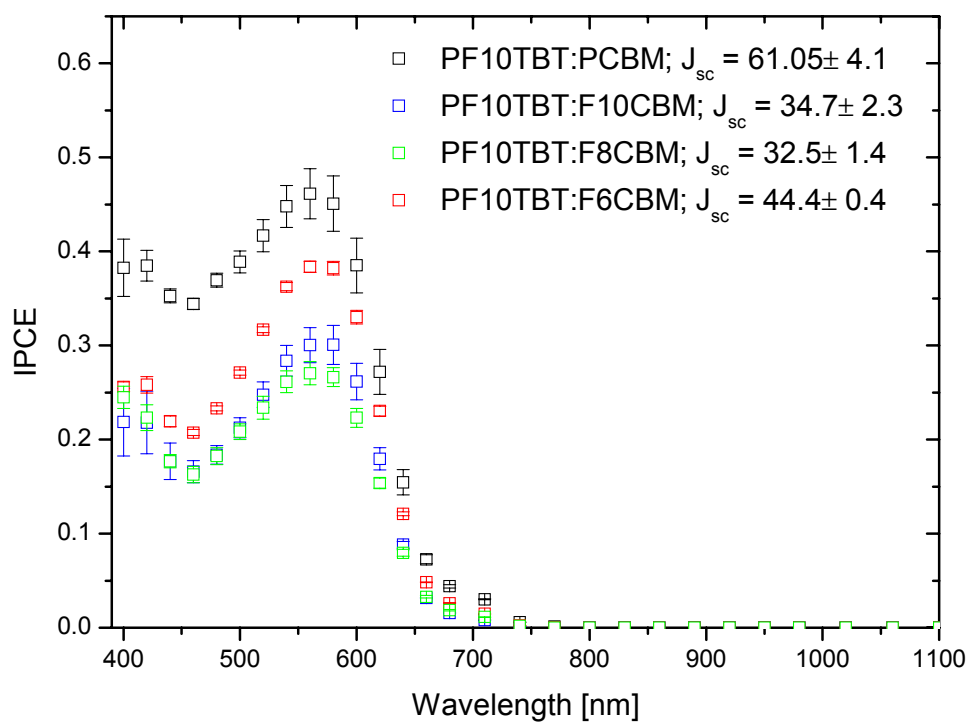


Figure S2. IPCE measurements of PF10TBT:fullerene solar cells. Averages over four devices on one substrate are taken. The error bars represent the spread in response for these devices, ranging from 9 mm² to 1 cm².

General

All reagents and solvents were purchased from Aldrich or Acros and used as received or purified using standard procedures. [60]Fullerene (99.5%) was purchased from Solenne BV and BuckyUSA and was used without further purification. Column chromatography was performed using silica gel (Aldrich 60, 230-240 mesh). Melting points were determined with a Mettler FP1 melting point apparatus equipped with a Mettler FP2 microscope. ^1H NMR and ^{13}C NMR were recorded on a Varian Unity Plus (500 MHz), on a Varian AMX400 (400 MHz) or a Varian VXR-200 (200 MHz) instrument as indicated in the specifications, at 298 K. Chemical shifts are donated in δ values (ppm) relative to TMS. FT-IR measurements were performed on a Nicolette Nexus FT-IR instrument. High Resolution Mass Spectroscopy (HRMS) was performed on a JEOL JMS 600 spectrometer. HPLC-MS analyses were performed on a Hewlett Packard Chemstation Agilent 1100 Series using an analytical Cosmosil Buckyprep Waters Type column (4.6 x 250 mm). Cyclic voltammetry was performed using an Autolab PGStat 100. All reactions were carried out in flame-dried glassware under an N_2 -atmosphere.

9,9-dihexyl-9H-fluorene (1): A suspension of fluorene (4.0 g, 24 mmol) and potassium hydroxide (13.0 g, 240 mmol, 10 eq.) in dimethyl sulfoxide (40 ml) was stirred at room temperature for 10 minutes and 1-bromooctane (9.9 g, 60 mmol, 2.5 eq.) was added using a syringe. The mixture was heated to 60°C and stirred for 5 days. The mixture was poured into water (100 ml) and extracted with ethyl acetate (3x 100 ml). The organic layers were combined and washed with brine (100 ml) and dried over sodium sulfate. The solvent was removed *in vacuo* and the crude product was purified by column chromatography (SiO_2 /heptane) to give the pure product as colorless oil (5.1 g, 15 mmol, 63%). FT-IR (neat) = ν (cm^{-1}): 3066 (m), 3039 (m), 3014 (m), 2954 (s), 2925 (s), 2852 (s), 1475 (w), 1465 (m), 1448 (s), 1376 (w), 773 (m), 736 (s). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.72 (d, $J = 7.2$, 2H), 7.50 – 7.28 (m, 6H), 2.19 – 1.83 (m, 4H), 1.32 – 0.96 (m, 12H), 0.78 (t, $J = 7.2$, 6H), 0.72 – 0.54 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 150.80, 141.22, 127.09, 126.79, 122.95, 119.75, 55.13, 40.55, 31.64, 29.87, 23.85, 22.73, 14.15. APCI-MS (m/z) = 335.27321, calculated $[\text{M}+\text{H}^+]$: 335.27333.

9,9-dioctyl-9H-fluorene (2): The alkylated fluorene **2** was prepared following the procedure described for **1** giving 7.4 g (19 mmol, 63%) of the pure product as colorless oil. FT-IR (neat) = ν (cm^{-1}): 3066 (m), 3039 (m), 3014 (m), 2954 (s), 2925 (s), 2852 (s), 1475 (w), 1465 (m), 1448 (s), 1376 (w), 773 (m), 736 (s). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.71 (d, $J = 6.6$, 2H), 7.60 – 7.10 (m, 6H), 2.16 – 1.77 (m, 4H), 1.39 – 0.95 (m, 20H), 0.83 (t, $J = 7.2$, 6H), 0.74 – 0.52 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 150.81, 141.22, 127.09, 126.79, 122.96, 119.75, 55.13, 40.51, 31.93, 30.19, 29.36, 23.88, 22.74, 14.23. APCI-MS (m/z) = 391.33585, calculated $[\text{M}+\text{H}^+]$: 391.33593.

9,9-didodecyl-9H-fluorene (3): The alkylated fluorene **3** was prepared following the procedure described for **1** giving 8.5 g (19 mmol, 64%) of the pure product as colorless oil. FT-IR (neat) = ν (cm^{-1}): 3066 (m), 3039 (m), 3014 (m), 2954 (s), 2925 (s), 2852 (s), 1475 (w), 1465 (m), 1448 (s), 1376 (w), 773 (m), 736 (s). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.71 (d, 2H), 7.42 – 7.18 (m, 6H), 2.04 – 1.86 (m, 4H), 1.36 – 0.94 (m, 28H), 0.86 (t, $J = 7.1$, 6H), 0.71 – 0.52 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 150.81, 141.22, 127.09, 126.79, 122.96, 119.75, 55.13, 40.51, 32.02, 30.19, 29.70, 29.66, 29.41, 29.41, 23.88, 22.81, 14.26. APCI-MS (m/z) = 447.39809, calculated $[\text{M}+\text{H}^+]$: 447.39853.

methyl 5-(9,9-dihexyl-9H-fluoren-2-yl)-5-oxopentanoate (4): A suspension of AlCl_3 (5.97 g, 44.83 mmol, 3 eq.) in 1,2-dichloroethane (100 ml) was cooled with an ice bath to 0°C and dialkylated fluorene **1** (5.0 g, 14.95 mmol) was added. After stirring the mixture for 10 minutes methyl 5-chloro-5-oxopentanoate (2.53 g, 15.69 mmol, 1.05 eq.) was slowly added with a syringe. The resulting dark green solution was allowed to warm up and was stirred at room temperature overnight. The mixture was poured onto crushed ice and the organic phase was separated. The aqueous layer was extracted with CH_2Cl_2 (2x 50 ml). The combined organic layers were washed with 2% aq. NaOH solution (50 ml), brine (50 ml), and dried over Na_2SO_4 . Evaporation of the solvent *in vacuo* yielded a pale yellow oil which was purified by column chromatography (SiO_2 /toluene) giving the pure keto-ester as colorless oil (3.61 g, 7.8 mmol, 52%). FT-IR (neat) = ν (cm^{-1}): 3066 (w), 2954 (s), 2929 (s), 2854 (s), 1739 (s), 1679 (s), 1606 (m), 1571 (w), 1465 (m), 1419 (m), 1367 (m), 1205 (m), 1006 (w), 740 (s). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 8.07 – 7.87 (m, 2H), 7.80 – 7.66 (m, 2H), 7.46 – 7.29 (m, 3H), 3.69 (s, 3H), 3.12 (t, $J = 7.1$, 2H), 2.49 (t, $J = 7.2$, 2H), 2.12 (p, $J = 7.1$, 2H), 2.07 – 1.89 (m, 4H), 1.16 – 0.92 (m, 12H), 0.74 (t, $J = 7.2$, 6H), 0.66 – 0.47 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 199.38, 173.90, 152.05, 151.15, 146.14, 139.86, 135.55, 128.48, 127.79, 127.09, 123.15, 122.31, 120.78, 119.55, 55.40, 51.68, 40.30, 37.70, 33.33, 31.56, 29.71, 23.81, 22.64, 19.63, 14.08. ESI-MS (m/z) = 485.30151, calculated $[\text{M}+\text{Na}^+]$: 485.30262.

methyl 5-(9,9-dioctyl-9H-fluoren-2-yl)-5-oxopentanoate (5): Keto-ester **5** was prepared following the procedure described for **4** except that the reaction mixture was refluxed overnight, giving 6.54 g (12.6 mmol, 82%) of the pure product as colorless oil. FT-IR (neat) = ν (cm^{-1}): 3066 (w), 2954 (s), 2929 (s), 2854 (s), 1739 (s), 1679 (s), 1606 (m), 1571 (w), 1465 (m), 1419 (m), 1367 (m), 1205 (m), 1006 (w), 740 (s). ^1H NMR (CDCl_3 , 400 MHz): δ (ppm) δ 8.02 – 7.90 (m, 2H), 7.82 – 7.68 (m, 2H), 7.42 – 7.31 (m, 3H), 3.70 (s, 3H), 3.12 (t, $J = 7.2$, 2H), 2.49 (t, $J = 7.2$, 2H), 2.12 (p, $J = 7.2$, 2H), 1.99 (dd, $J = 14.2, 7.2$, 4H), 1.28 – 0.93 (m, 20H), 0.80 (t, $J = 7.1$, 6H), 0.67 – 0.46 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 199.35, 173.90, 152.07, 151.16, 146.15, 139.88, 135.57, 128.49, 127.80, 127.10, 123.17, 122.32, 120.78, 119.55, 55.41, 51.68, 40.29, 37.70, 33.34, 31.85, 30.04, 29.30, 23.85, 22.68, 19.63, 14.17. ESI-MS (m/z) = 541.36365, calculated $[\text{M}+\text{Na}^+]$: 541.36522.

methyl 5-(9,9-didodecyl-9H-fluoren-2-yl)-5-oxopentanoate (6): Keto-ester **6** was prepared following the procedure described for **4** except that the reaction mixture was refluxed overnight, yielding 8.14 g (14.2 mmol, 84%) of the pure product as colorless oil. FT-IR (neat) = ν (cm^{-1}): 3066 (w), 2954 (s), 2929 (s), 2854 (s), 1739 (s), 1679 (s), 1606 (m), 1571 (w), 1465 (m), 1419 (m), 1367(m), 1205 (m), 1006 (w), 740 (s). ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.99 (s, 1H), 7.95 (d, $J = 7.9$, 1H), 7.76 – 7.67 (m, 2H), 7.38 – 7.27 (m, 3H), 3.71 (s, 3H), 3.10 (t, $J = 7.0$, 2H), 2.47 (t, $J = 7.0$, 2H), 2.11 (p, $J = 7.0$, 2H), 2.07 – 1.90 (m, 4H), 1.32 – 0.91 (m, 28H), 0.91 (t, $J = 7.0$, 6H), 0.69 – 0.46 (m, 4H). ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 198.97, 173.62, 151.90, 151.01, 146.00, 139.76, 135.49, 128.35, 127.68, 126.98, 122.99, 122.21, 120.66, 119.42, 55.27, 51.43, 40.19, 37.55, 33.16, 31.85, 29.95, 29.52, 29.49, 29.25, 29.24, 23.75, 22.64, 19.52, 14.08. ESI-MS (m/z) = 597.42596, calculated $[\text{M}+\text{Na}^+]$: 597.42782.

9,9-dihexyl-9H-fluoren-2-yl-methylbutyrate-p-tosylhydrazone (7): Methyl 5-(9,9-dihexyl-9H-fluoren-2-yl)-5-oxopentanoate (**4**) (2.86 g, 6.18 mmol) and p-tosylhydrazide (1.38 g, 7.42 mmol, 1.2 eq.) were dissolved in toluene (80 ml). The resulting solution was refluxed overnight using a Dean-Stark setup. After cooling to room temperature the white precipitate was filtered off. The solution was concentrated *in vacuo*. The remaining yellow oil was recrystallized from methanol to yield 2.35 g (3.7 mmol, 60%) of the product as pale yellow crystals. FT-IR (neat) = ν (cm^{-1}): 3182 (s), 2954 (s), 2921 (s), 2854 (s), 1716 (s), 1600 (m), 1467 (m), 1438 (m), 1367 (m), 1322 (m), 1268 (m), 1224 (m), 1172 (s), 1078 (m), 1022 (m), 995 (m), 937 (m), 873 (m), 815 (m), 746 (m), 667 (m), 553 (s). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 9.10 (s, 1H), 7.96 (d, $J = 8.3$, 2H), 7.74 – 7.50 (m, 4H), 7.40 – 7.21 (m, 5H), 3.81 (s, 3H), 2.68 (t, 2H), 2.47 – 2.28 (m, 5H), 1.96 (dd, $J = 11.3$, 5.4, 4H), 1.81 – 1.64 (m, 2H), 1.19 – 0.90 (m, 12H), 0.75 (t, $J = 7.1$, 6H), 0.66 – 0.49 (m, 4H). ^{13}C NMR (50 MHz, CDCl_3): δ (ppm) 174.90, 154.39, 151.37, 151.00, 143.85, 142.77, 140.39, 136.12, 134.98, 129.52, 128.28, 127.67, 126.97, 125.38, 123.06, 120.58, 120.15, 119.55, 55.19, 52.55, 40.45, 32.25, 31.61, 29.84, 26.22, 23.83, 22.70, 21.72, 21.22, 14.13. APCI-MS (m/z) = 631.35686, calculated $[\text{M}+\text{H}^+]$: 631.35641. Melting Point: 94.0 – 96.0°C.

9,9-dioctyl-9H-fluoren-2-yl-methylbutyrate-p-tosylhydrazone (8): Tosylhydrazone **8** was prepared following the procedure described for **7** except that the reaction was stopped after 5 hours instead of reacting overnight, yielding 6.68 g (9.7 mmol, 92%) of the pure product as pale yellow crystals. FT-IR (neat) = ν (cm^{-1}): 3118 (s), 2952 (s), 2925 (s), 2854 (s), 1710 (s), 1596 (m), 1465 (m), 1438 (m), 1369 (m), 1321 (m), 1265 (m), 1230 (m), 1170 (s), 1022 (m), 995 (m), 937 (m), 873 (m), 815 (m), 746 (m), 667 (m), 553 (s). ^1H NMR (200 MHz, CDCl_3): δ (ppm) 9.13 (s, 1H), 7.97 (d, $J = 8.3$, 2H), 7.73 – 7.51 (m, 4H), 7.37 – 7.27 (m, 5H), 3.81 (s, 3H), 2.68 (t, 2H), 2.45 – 2.26 (m, 5H), 2.05 – 1.85 (m, 4H), 1.84 (t, 2H), 1.32 – 0.90 (m, 20H), 0.80 (t, $J = 6.6$, 6H), 0.69 – 0.40 (m, 4H). ^{13}C NMR (50 MHz, CDCl_3): δ (ppm) 174.91, 154.31, 151.38, 151.01, 143.84, 142.77, 140.40, 136.15, 134.99, 129.52, 128.29, 127.68, 126.97, 125.38, 123.08, 120.58, 120.16, 119.56, 55.20, 52.56, 40.45, 32.25, 31.90, 30.21, 29.39, 26.21, 23.91, 22.73, 21.73, 21.22, 14.21. APCI-MS (m/z) = 687.41944, calculated $[\text{M}+\text{H}^+]$: 687.41901. Melting Point: 99.5 – 101.0°C.

9,9-didodecyl-9H-fluoren-2-yl-methylbutyrate-p-tosylhydrazone (9): Tosylhydrazone **9** was prepared following the procedure described for **7** except that the reaction was stopped after 4 hours instead of reacting overnight, giving 7.14 g (9.6 mmol, 84%) of the pure product as pale yellow crystals. FT-IR (neat) = ν (cm^{-1}): 3108 (s), 2952 (s), 2919 (s), 2854 (s), 1708 (s), 1596 (m), 1469 (m), 1438 (m), 1369 (m), 1322 (m), 1265 (m), 1230 (m), 1170 (s), 1022 (m), 995 (m), 937 (m), 873 (m), 815 (m), 746 (m), 667 (m), 553 (s). ^1H NMR (200 MHz, CDCl_3): δ (ppm) 9.13 (s, 1H), 7.97 (d, $J = 8.2$, 2H), 7.74 – 7.50 (m, 4H), 7.42 – 7.27 (m, 5H), 3.81 (s, 3H), 2.79 (t, 2H), 2.44 – 2.28 (m, 5H), 2.03 – 1.84 (m, 4H), 1.84 – 1.61 (m, 2H), 1.37 – 0.92 (m, 28H), 0.84 (t, $J = 6.5$, 6H), 0.73 – 0.43 (m, 4H). ^{13}C NMR (50 MHz, CDCl_3): δ (ppm) 174.90, 154.37, 151.38, 151.02, 143.83, 142.78, 140.39, 136.14, 134.97, 129.52, 128.29, 127.68, 126.97, 125.39, 123.08, 120.59, 120.15, 119.56, 55.20, 52.55, 40.46, 32.25, 32.00, 30.23, 29.74, 29.65, 29.45, 29.40, 26.22, 23.93, 22.78, 21.73, 21.23, 14.24. APCI-MS (m/z) = 743.48216, calculated $[\text{M}+\text{H}^+]$: 743.48161. Melting Point: 74.5 – 76.0°C.

9,9-dihexyl-9H-fluoren-2-yl- C_{60} -butyric-acid methylester (10): A mixture of 9,9-dihexyl-9H-fluoren-2-yl-methylbutyrate-p-tosylhydrazone **7** (400 mg, 0.64 mmol, 1.1 eq.) and sodium methoxide (36 mg, 0.66 mmol, 1.1 eq.) was dissolved in dry pyridine (10 ml) and stirred at room temperature for 30 minutes. Then a degassed solution of C_{60} (427 mg, 0.59 mmol) in *ortho*-dichlorobenzene (50 ml) was added. The mixture was heated to 90°C and irradiated with a 150 W Na-lamp. The solution was concentrated *in vacuo* after reacting overnight. The product was purified on a SiO_2 column. The unreacted C_{60} was eluted with CS_2 and then the product with a 1:1 mixture of toluene and cyclohexane. After removal of the eluent *in vacuo* a dark solid remained. The solid was precipitated from *ortho*-dichlorobenzene in methanol and subsequently centrifuged. The remaining brown pellet was washed twice with methanol and dried *in vacuo* at 40°C overnight. Yielding 361 mg (0.3 mmol, 52%) of the product as a brown solid. FT-IR (neat) = ν (cm^{-1}): 2921 (s), 2850 (s), 1743 (s), 1463 (m), 1432 (m), 1241 (w), 1186 (m), 742 (m), 586 (w), 574 (w), 553 (w), 526 (s), 441 (w). ^1H NMR (500 MHz, $\text{CS}_2/\text{D}_2\text{O}$): δ (ppm) δ 8.16 – 8.07 (m, 3H), 8.00 – 7.95 (m, 1H), 7.62 – 7.55 (m, 3H), 3.89 (s, 3H), 3.32 – 3.18 (m, 2H), 2.78 (t, $J = 7.3$ Hz, 2H), 2.55 – 2.42 (m, 2H), 2.40 – 2.19 (m, 4H), 1.56 – 0.69 (m, 22H). ^{13}C NMR (125 MHz, $\text{CS}_2/\text{D}_2\text{O}$): δ (ppm) 171.46, 150.89, 150.42, 148.92, 147.80, 145.94, 145.27, 145.25, 145.13, 145.04, 144.87, 144.72, 144.68, 144.58, 144.55, 144.06, 143.87, 143.80, 143.22, 143.10, 143.04, 143.02, 142.35, 142.22, 142.03, 141.33, 141.16, 140.80, 140.49, 138.24, 137.56, 135.12, 130.75, 127.78, 127.24, 127.16, 122.81, 120.27, 119.94, 80.19, 55.06, 52.44, 51.14, 40.98, 33.78, 33.70, 32.25, 30.46, 24.54, 23.46, 22.90, 14.73. APCI-MS (m/z) = 1167.32692, calculated $[\text{M}+\text{H}^+]$: 1167.32576.

9,9-dioctyl-9H-fluoren-2-yl- C_{60} -butyric-acid methylester (11): Methanofullerene **11** was prepared following the procedure described for **10**, yielding 2.99 g (2.45 mmol, 64%) of the pure product as a brown solid. FT-IR (neat) = ν (cm^{-1}): 2921 (s), 2850 (s), 1741 (s), 1463 (m), 1432 (m), 1259 (w), 1187 (m), 740 (m), 584 (w), 574 (w), 553 (w), 526 (s), 480 (w), 447 (w). ^1H NMR ($\text{CS}_2/\text{D}_2\text{O}$, 500 MHz): δ (ppm) 8.10 – 7.99 (m, 3H), 7.93 – 7.88 (m, 1H), 7.56 – 7.48 (m, 3H), 3.82 (s, 3H), 3.27 – 3.10 (m, 2H), 2.71 (t, $J = 7.1$ Hz, 2H), 2.50 – 2.38 (m, 2H), 2.34 – 2.10 (m, 4H), 1.60 – 0.60 (m, 30H). ^{13}C NMR ($\text{CS}_2/\text{D}_2\text{O}$, 125 MHz): δ (ppm) 171.49, 150.89, 150.42, 148.94, 147.81, 145.96, 145.28, 145.25, 145.12, 145.05, 144.87, 144.72, 144.71, 144.58,

144.55, 144.06, 143.87, 143.81, 143.23, 143.11, 143.09, 143.04, 143.03, 142.35, 142.22, 142.03, 141.32, 141.16, 140.80, 140.49, 138.25, 137.56, 135.11, 130.75, 127.79, 127.24, 127.20, 122.82, 120.29, 119.97, 80.12, 55.05, 52.46, 51.17, 41.00, 33.75, 33.70, 32.45, 30.86, 30.01, 24.66, 23.47, 22.90, 14.89. APCI-MS (m/z) = 1223.38857, calculated $[M+H]^+$: 1223.38836.

9,9-didecyl-9H-fluoren-2-yl- C_{61} -butyric-acid methylester (12): Methanofullerene **12** was prepared following the procedure described for **10**, yielding 4.30 g (3.36 mmol, 56%) of the pure product as a brown solid. FT-IR (neat) = ν (cm^{-1}): 2921 (s), 2850 (s), 1741 (s) 1463 (m), 1432 (m), 1249 (w), 1187 (m), 742 (m), 584 (w), 574 (w), 553 (w), 526 (s), 480(w), 435 (w). ^1H NMR ($\text{CS}_2/\text{D}_2\text{O}$, 500 MHz): δ (ppm) 8.13 – 8.00 (m, 3H), 7.94 – 7.88 (m, 1H), 7.59 – 7.49 (m, 3H), 3.83 (s, 3H), 3.30 – 3.10 (m, 2H), 2.72 (t, $J = 7.1$ Hz, 2H), 2.51 – 2.38 (m, 2H), 2.35 – 2.11 (m, 4H), 1.63 – 0.57 (m, $J = 168.1$ Hz, 38H). ^{13}C NMR ($\text{CS}_2/\text{D}_2\text{O}$, 125 MHz): δ (ppm) 171.48, 150.88, 150.41, 148.93, 147.80, 145.94, 145.28, 145.25, 145.10, 145.05, 144.87, 144.86, 144.72, 144.69, 144.58, 144.55, 144.06, 143.87, 143.80, 143.22, 143.10, 143.04, 143.02, 142.35, 142.22, 142.02, 141.31, 141.16, 140.79, 140.49, 138.25, 137.55, 135.11, 130.74, 127.78, 127.24, 127.20, 122.82, 120.28, 119.95, 80.18, 55.04, 52.44, 51.16, 40.99, 33.74, 33.69, 32.53, 30.86, 30.35, 30.24, 29.97, 24.65, 23.52, 22.89, 14.87. APCI-MS (m/z) = 1279.45150, calculated $[M+H]^+$: 1279.45096.

Crystallographic data

The position of the electrophilic substitution on the fluorene moiety was confirmed by x-ray crystal structure. Suitable crystals of the hexyl-substituted tosylhydrazone (**7**) were obtained by recrystallization from a pentane/methanol mixture. The crystal structure shows that the fluorene was acylated at the 2-position (C14).

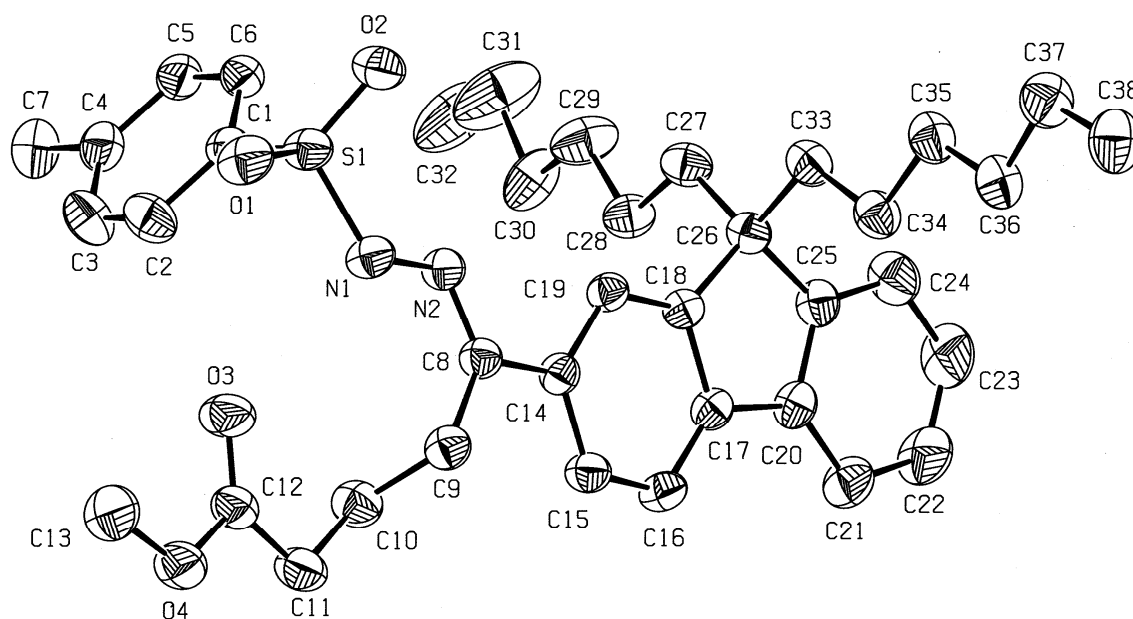


Figure S3: X-ray crystal structure of 9,9-dihexyl-9H-fluorene-2-yl-methylbutyrate-p-tosylhydrazone (**7**)

9,9-dihexyl-9H-fluorene-2-yl-methylbutyrate-p-tosylhydrazone, $C_{38}H_{50}N_2O_4S$, $M_r = 630.89$, triclinic, $P-1$, $a = 11.464(3)$, $b = 12.033(3)$, $c = 14.111(4)$ Å, $\alpha = 83.464(4)^\circ$, $\beta = 81.891(4)^\circ$, $\gamma = 69.071(3)^\circ$, $V = 1795.7(8)$ Å³, $Z = 2$, $D_x = 1.167$ g cm⁻³, $F(000) = 680$, $\mu = 1.3$ cm⁻¹, $\lambda(\text{MoK}\alpha) = 0.71073$ Å, $T = 293(1)$ K, 13180 reflections measured, $Goof = 1.017$, $wR(F^2) = 0.1688$ for 6447 unique reflections and 410 parameters, and $R(F) = 0.0563$ for 4195 reflections obeying $F_o \geq 4.0 \sigma(F_o)$ criterion of observability. The asymmetric unit consists of one molecule of the title compound.