Supporting Information (SI)

1. Material and methods

Instruments and measurements. Nucelar Magnetic Resonance (NMR) spectra were recorded on a Bruker AMX 500 (^{13}C-NMR: 125 MHz; ^{1}H-NMR: 500 MHz) or an Avance 400 Spectrometer (^{13}C-NMR: 100 MHz; ^{1}H-NMR: 400 MHz). Chemical shift values (δ) are expressed in parts per million (ppm) using residual solvent protons (δ= 5.91 (d_2-TCE) and 7.26 ($CDCl_3$) for ^{1}H-NMR spectra and δ= 74.20 (d_2-TCE) and 77.16 ($CDCl_3$) for ^{13}C-NMR spectra) as internal standard. Coupling constants *J* relate to proton-proton couplings. The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), and m (multiplet). The assignments of the protons correspond to Th-H (thiophene-proton), CHO (aldehyde proton), vinyl-H (proton of the vinyl group), α- ζ: protons of the alkyl chains.

Thin layer chromatography was carried out on aluminum plates, pre-coated with silica gel, Merck Si60 F_{254}. Preparative column chromatography was performed on glass columns packed with silica gel 60 M (Macherey-Nagel) particle size 0.04-0.063 mm or silica gel 60 (Macherey-Nagel) particle size 0.063-0.2 mm. Melting points were determined using a Mettler Toledo DSC 823e under Ar flow (heating rate 10 °C/min) or a Büchi Melting Point M-565 (not corrected). Gas chromatography-mass spectrometry (GC-MS) measurements were performed on a Shimadzu GCMS-QP2010 SE. Matrix-assisted-laser desorption-ionisation time-of-flight (MALDI-TOF) mass spectra were found on Bruker Daltonik Reflex III and high resolution MALDI mass spectra were performed on a Bruker SolariX using trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. CI mass spectra were recorded on a Finnigan MAT, SSQ-7000. EI mass spectra were recorded on a Varian Saturn 2000 GC-MS. High resolution APCI spectra were performed on a Bruker SolariX using acetonitrile as solvent.

Optical measurements in solution were carried out in 1 cm cuvettes with Merck Uvasol grade solvents. Absorption spectra were recorded on a Perkin Elmer Lambda 19 spectrometer and corrected fluorescence spectra were recorded on a Perkin Elmer LS 55 fluorescence spectrometer. Cyclic voltammetry (CV) experiments were performed with a computer-controlled Autolab PGSTAT30 potentiostat in a three-electrode single-compartment cell (2 mL). The platinum working electrode consisted of a platinum wire sealed in a soft glass tube with a surface of A = 0.785 mm^2, which was polished down to

0.25 µm with Buehler polishing paste prior to use to guarantee reproducible surfaces. The counter electrode consisted of a platinum wire and the reference electrode was an Ag/AgCl reference electrode. All potentials were internally referenced to the ferrocene/ferricenium couple (Fc/Fc^+). For the measurements, concentrations of 10^{-3} M of the electroactive species were used in freshly distilled and deaerated dichloromethane (Lichrosolv, Merck) purified with a Braun MB-SPS-800 and 0.1 M $(n\text{-}Bu)_4NPF_6$ (Fluka; recrystallized twice from ethanol).

Device fabrication of organic solar cells was performed with indium tin oxide (ITO) patterned glass substrates (15 Ω cm^{-2}, from Naranjo Substrates), which were precleaned with acetone, Mucasol soap solution, and isopropanol, before treated in a UV-ozone cleaner for 30 min. PEDOT:PSS was spin-coated at 3000 rpm to obtain thin films of 20-30 nm thickness. The active layer solutions (10 mg/mL to 20 mg/mL in chloroform, chlorobenzene or tetrachloroethane) were deposited by spin-coating at various spin speeds. Thin films of lithium fluoride (LiF, 0.7 nm) and aluminum (Al, 100-120 nm) were deposited by high-vacuum evaporation at pressures below 3 x 10^{-6} mbar (Nano 36, from Kurt J. Lesker Co.). Solvent vapor annealing (SVA) was performed by a literature known procedure.[1] One substrate contained four photoactive areas of 0.09 and 0.16 cm^2. *J-V*-characteristics of the prepared devices were obtained by using a solar simulator (Oriel Instruments, class AAA, AM 1.5G, 10 $mWcm^{-2}$). Apart from LiF and aluminum deposition, processing and characterization of the solar cells were performed under ambient conditions.

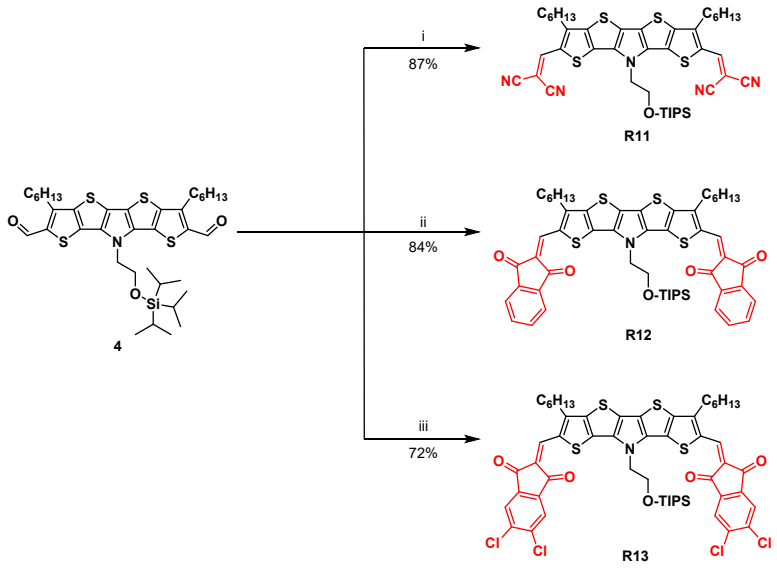
Materials. Toluene (Sigma Aldrich), tetrahydrofurane (THF) (Carl Roth GmbH), dichloromethane, DMF (VWR), and diethyl ether (VWR) were dried and purified by a MB SPS-800 (MBraun). Dichloromethane (DCM), chloroform (CF), dimethylformamide (DMF), ethylacetate (EA), petroleum ether (PE), methanol, diethyl ether (Et_2O), quinoline, hydrochloric acid (HCl), and acetone were purchased from VWR, chlorobenzene (CB) from Merck and the solvents were distilled prior to use if necessary. Fluka delivered tetrachloroethylene and anisole. 3-Ethylheptanoylchloride, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide-hydrochlorid EDCxHCl, o-dichlorobenzene (oDCB), palladium(II) acetate ($Pd(OAc)_2$), N-formylpiperidine (N-Fpip), carbon disulphide (CS_2), cesium carbonate, bis(dibenzylideneacetone)palladium(0) ($Pd(dba)_{2)}$, triisopropylsilylchloride, malonodinitrile, sodium *tert*-butanolate (NaO^tBu), and tetrabutylammonium fluoride (TBAF) solution (1M in THF) were purchased from Sigma Aldrich. Aluminum chloride, 4-(dimethylamino)pyridine, 1,3-indandione (IND), piperidine, ferrocene (Fc), 1,2-dichloroethane (DCE), and 1,1,2,2-tetrachloroethane (TCE) were bought from Alfa Aesar. Ethylthioglycolate, pyridine, copper (II) chloride, N-bromosuccinimide (NBS), potassium acetate (KOAc), phosphoryl chloride, sodium hydroxide (NaOH), ammonium acetate (NH_4OAc), chlorobenzene (CB), potassium hydroxide (KOH), triethylamine (TEA), lithium hydroxide (LiOH), triisopropylsilyl chloride, diisopropylamine, and copper powder were purchased from Merck. *n*-Butyl lithium (*n*-BuLi) (1.6 M in hexane) was

purchased from Acros Organics and 1,1'-bis(diphenylphosphino)ferrocene from Fluorochem. Calcium hydride was bought from TCI and magnesium sulfate from Grüssing. [6,6]-Phenyl-C_{61}-butyric acid and [6,6]-phenyl-C_{61}-butyric acid methyl ester were purchased from SolenneBV. Poly(3,4-ethylenedioxy-thiophene)polystyrolsulfonate (PEDOT-PSS, Clevios P, VP. AI 4038 aqueous solution) was purchased from Ossila, 1,8-diiodooctane (DIO) from Alfa Aesar, ultrapure aluminum (Al) (99.98%) from Umicore, and lithium fluoride (LiF) from ACROS.

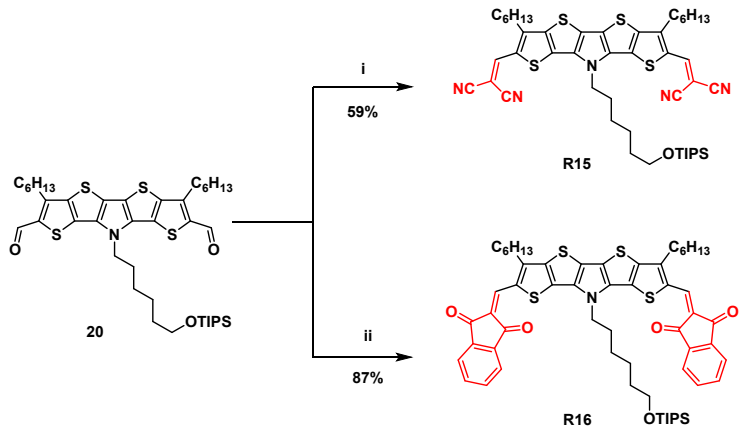
Triisopropylsilyl (TIPS)-protected monoethanolamine **2**,[1] dihexyl-bithienothiophene **1**,[2] 5,6-di-chloroindene-1,3-dione (Cl_2-IND),[3] 2-ethylhexyl (EtHex) carbonyl chloride **8**,[4] TIPS-protected hexan-olamine **18**, [5] iodothiophene aldehyde **24**,[6] and dicyanomethylene-3-indanone (DCI)[7] were synthesi-zed according to internally used literature-known procedures.

2. Synthetic procedures

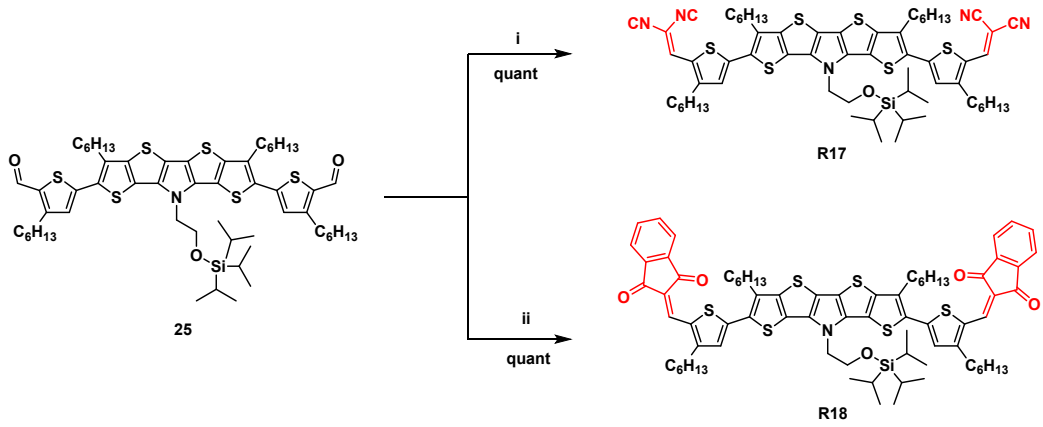
Synthesis schemes for reference derivatives R11-R18. TIPS-protected dialdehyde **4** was additionally reacted with the three acceptors dicyanovinyl (DCV), 1,3-indandione (IND), and 5,6-dichloro-1,3-indandione (Cl_2-IND) in Knoevenagel condensation reactions to give reference derivatives **R11**-**R13** in 72% to 87% yield which represent the donor unit of the dyads without appended fullerene (Scheme S3). Reference derivative **R14** is not presented due to severe problems in work-up and purification.



Scheme S1: Synthesis of TIPS-protected SN5'-derivatives **R11-R13**: i) malononitrile, DCE, NH_4OAc, 70 °C, 4 d; ii) IND, DCE, piperidine, rt, 24 h; iii) Cl_2-IND, CF, pyridine, 70 °C, 4 d.



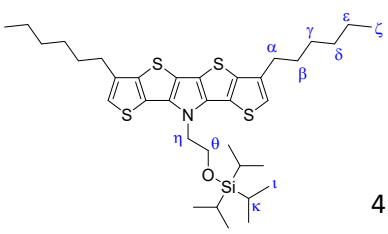
Scheme S2: Synthesis of TIPS-protected SN5'-derivatives **R15** and **R16**: i) malononitrile, DCE, NH_4OAc, 80 °C, 5d, ii) IND, DCE, piperidine,48 h, rt.



Scheme S3: Syntheses of the TIPS-protected SN5'-derivatives **R17, R18**: i) malononitrile, NH_4OAc, DCE, 80 °C, 16 h, ii) IND, DCE, piperidine, rt, 16 h.

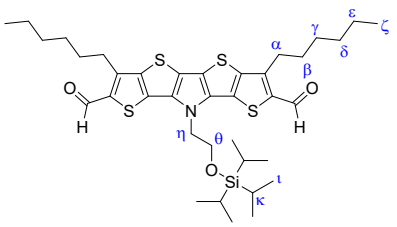
Synthetic details.

3,6-Dihexyl-9-{2-[(triisopropylsilyl)oxy]ethyl}-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno-[2,3-d]pyrrole ***3***. 3,3'-Dibromo-6,6'-bis(2-ethylhexyl)-2,2'-bithieno[3,2-*b*]thiophene (500 mg, 0.83 mmol), $Pd(dba)_2$ (47.6 mg, 82.7 µmol), dppf (183 mg, 0.33 mmol), and NaO^tBu (795 mg, 8.27 mmol) were dissolved in dry and argon purged toluene (13.2 mL). The mixture was purged again with argon for 30 min until 2-[(triisopropylsilyl)oxy]ethan-1-amine (224 µL, 0.99 mmol) was added and the mixture was purged again. The reaction mixture was stirred for 23 h at 110 °C. Afterwards, the solvent was removed and column chromatography over silica gel (DCM/PE 1:4) delivered SN5'-derivative **3** (505 mg, 0.77 mmol, 92% yield) as a light yellow solid. Mp 48.0-51.1 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 6.87 (s, 2H, Th-H), 4.49 (t, $^3J_{H\vartheta\text{-}H\eta}$ = *6.2 Hz*, 2H, Hθ), 4.13 (t, $^3J_{H\eta\text{-}H\vartheta}$ = *6.2 Hz*, 2H, Hη), 2.74 (t, $^3J_{H\alpha\text{-}H\beta}$ = *7.6 Hz*, 4H, Hα), 1.83-1.75 (m, 4H, Hβ), 1.43-1.23 (m, 12 H, Hγ-Hε), 0.99-0.86 (m, 27H, Hζ, Hκ, Hι); ^{13}C-NMR (400 MHz, $CDCl_3$): δ [ppm] = 139.0, 136.6, 135.4, 123.2, 118.1, 117.4, 63.2, 50.5, 31.8, 29.6, 29.2, 28.9, 22.8, 17.8, 14.3, 12.0; HR-MS (FTICR-MALDI): M^+ calculated for

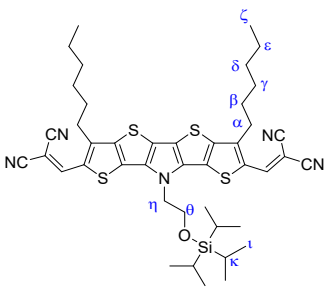


$C_{35}H_{53}NOS_4Si$: m/z = 659.2774; found: m/z = 659.2762 (δm/m = 1.76 ppm).

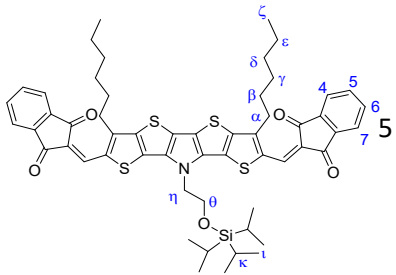
*3,6-Dihexyl-9-{2-[(triisopropylsilyl)oxy]ethyl}-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno-[2,3-d]pyrrole-2,7-dicarbaldehyde **4**.* Heteroacene **3** (450 mg, 682 µmol) was dissolved in argon purged, dry THF (8 mL) and cooled to -78 °C. Afterwards, *n*-BuLi (1.6 M-solution, 1.70 mL, 2.73 mmol) was added dropwise within 20 min. The mixture was stirred for 3 h at -78 °C and then quenched with *N*-formylpiperidine (605 µL, 5.45 mmol). After the solution was stirred for 18 h and thawed to room temperature (r.t.), water was added and the mixture was extracted two times with DCM. The organic phases were dried over magnesium sulfate and column chromatography over flash silica gel (DCM/3% EA) delivered dialdehyde **4** (363 mg, 507 µmol, 74.4% yield) as a yellow solid. Mp 230.7-235.1 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 10.07 (s, 2H, C*H*O), 4.53 (t, $^3J_{Hϑ-Hη}$ *= 5.2 Hz*, 2H, Hθ), 4.12 (t, $^3J_{Hη-Hϑ}$*= 5.2 Hz*, 2H, Hη), 3.11(t, $^3J_{Hα-Hβ}$ *= 7.6 Hz*, 4H, Hα), 1.88-1.80 (m, 4H, Hβ), 1.44-1.25 (m, 12H, Hγ-Hε), 0.90-0.87 (m, 6H, Hζ), 0.85-0.78 (m, 3H, Hκ), 0.73-0.71 (m, 18H, Hι). ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 181.8, 146.6, 141.5, 137.3, 137.1, 129.3, 122.0, 62.9, 50.9, 31.7, 30.3, 29.2, 28.1, 22.7, 17.6, 14.2, 11.8. HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{37}H_{53}NO_3S_4Si$: m/z = 715.2672; found: m/z = 715.2654 (δm/m = 2.56 ppm).



*2,2'-{{3,6-Dihexyl-9-{2-[(triisopropylsilyl)oxy]ethyl}-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]pyrrole-2,7-diyl}bis(methaneylylidene)} dimalononitrile **R11**.* Aldehyde **4** (50.0 mg, 69.8 µmol) and malonodinitrile (92.2 mg, 1.40 mmol) were dissolved in DCE (15 mL) and ammonium acetate (215 mg, 2.79 mmol) was added as a base. The mixture was heated to 70 °C and stirred for 4 days. Subsequently, the solvent was removed under reduced pressure and column chromatography over flash silica gel (DCM) afforded SN5'-derivatve **12** (49.5 mg, 60.9 µmol, 87.3%) as a dark solid with green metallic gloss. **R11** was dissolved in DCM and precipitated from methanol. Mp 308.1-311.6 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.88 (s, vinyl-H, 2H), 4.52 - 4.51 (m 2H, Hθ) 4.10 (t, $^3J_{Hη-Hϑ}$*= 4.6 Hz*, 2H, Hη), 2.93 (t, $^3J_{Hα-Hβ}$ *= 7.7 Hz*, 4H, Hα), 1.78-1.71 (m, 4H, Hβ), 1.40-1.23 (m, 12H, Hγ-Hε), 0.92-0.88 (m, 6H, Hζ), 0.70-0.68 (m, 21H, Hι, Hκ); ^{13}C-NMR (400 MHz, $CDCl_3$): δ [ppm] = 148. 5, 147.7, 142. 6, 138.2, 130.6, 130.0, 123.9, 115.3, 114.0, 62.8, 51.3, 31.6, 30.5, 29.3, 28.9, 22.7, 17.6, 14.2, 11.8; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{43}H_{53}N_5OS_4Si$: m/z = 811.2897; found: m/z = 811.2899 (δm/m = 0.26 ppm).

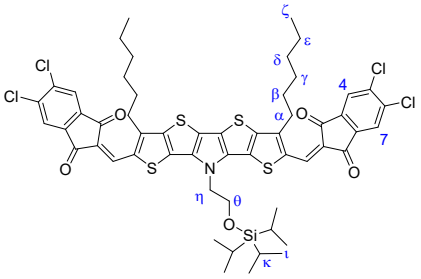


2,2'-{{3,6-Dihexyl-9-{2-[(triisopropylsilyl)oxy]ethyl}-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]pyrrole-



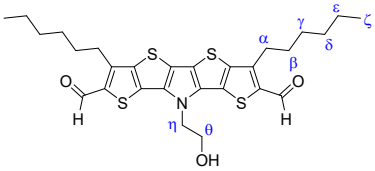
2,7-diyl}bis(methaneylylidene)}bis(1H-indene-1,3(2H)-dione) ***R12****.* Aldehyde **4** (40.0 mg, 55.9 µmol) and 1,3-indandione (32.7 mg, 223 µmol) were dissolved in DCE (12 mL) and three drops of piperidine were added. The mixture was stirred for 18 h at r.t. Afterwards, the solvent was removed under reduced pressure and column chromatography over flash silica gel (DCM/EA 95/5) afforded SN5'-derivative **R12** (45.7 mg, 47.0 µmol, 84.1%) as a dark blue solid that was precipitated and filtered from methanol. Mp 203.5-206.3 °C; ^{1}H-NMR (500 MHz, d_2-TCE): δ [ppm] = 8.01 (s, 2H, vinyl-H), 7.90-7.84 (m, 4H, H4, H7), 7.68-7.64 (m, 4H, H5, H6), 4.72 (t, $^{3}J_{Hϑ\text{-}Hη}$ *= 5.1Hz*, 2H, Hθ), 4.22 (t, $^{3}J_{Hη\text{-}Hϑ}$*= 5.1 Hz*, 2H, Hη), 3.04 (t, $^{3}J_{Hα\text{-}Hβ}$ *= 7.7 Hz*, 4H, Hα), 1.81-1.75 (m, 4H, Hβ), 1.41-1.23 (m, 12H, Hγ-Hε), 0.86 (t, $^{3}J_{Hζ\text{-}Hε}$*= 7.1 Hz*, 6H, Hζ), 0.79-0.66 (m, 21H, Hι, Hκ); ^{13}C-NMR (126 MHz, d_2-TCE , UDEFT): δ [ppm] = 190.3, 189.5, 149.9, 143.1, 142.3, 140.7, 138.8, 134.8, 134.6, 133.3, 133.2, 132.6, 123.7, 122.8, 122.8, 122.2, 63.2, 51.5, 31.7, 30.7, 29.4, 29.2, 22.7, 17.7, 14.2, 12.1; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{55}H_{61}NO_5S_4Si$: m/z = 971.3196; found: m/z = 971.3197 (δm/m = 0.03 ppm).

2,2'-{[3,6-Dihexyl-9-(2-[(triisopropylsilyl)oxy)ethyl]-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]-thieno[2,3-d]pyrrole-2,7-diyl]bis(methaneylylidene)}bis[5,6-dichloro-1H-indene-1,3(2H)-dione] ***R13****.* Aldehyde **4** (10.0 mg, 14.0 µmol) and 5,6-dichloro-1H-indene-1,3(2H)-dione (12.0 mg, 55.9 µmol) were dissolved in chloroform (3 mL) and some drops of pyridine were added. After 3 days of stirring at 70 °C, 5,6-dichloro-1H-indene-1,3(2H)-dione (12.0 mg, 55.9 µmol) was added once again. After another day of stirring at 70 °C, the solvent was removed under reduced pressure and column chromatography over flash silica gel (DCM) afforded SN5'-derivative **R13** (11.1 mg, 10.0 µmol, 71.6%) as a dark solid which was precipitated and filtered from methanol. Mp 290.5-293.0 °C; ^{1}H-NMR (500 MHz, d_2-TCE): δ [ppm] = 7.90 (s, 2H, vinyl-H), 7.80-7.78 (m, 4H, H4, H7), 4.66 (t, $^{3}J_{Hϑ\text{-}Hη}$ *= 4.8 Hz*, 2H, Hθ), 4.16 (t, $^{3}J_{Hη\text{-}Hϑ}$*= 5.1 Hz*, 2H, Hη), 2.97 (t, $^{3}J_{Hα\text{-}Hβ}$ *= 7.6 Hz*, 4H, Hα), 1.77-1.71 (m, 4H, Hβ), 1.44-1.23 (m, 12H, Hγ-Hε), 0.86 (t, $^{3}J_{Hζ\text{-}Hε}$*= 6.9 Hz*, 6H, Hζ), 0.74-0.67 (m, 3H, Hκ), 0.62-0.61 (m, 21H, Hι); ^{13}C-NMR (126 MHz, d_2-TCE , UDEFT): δ [ppm] = 187.9, 187.2, 150.9, 143.5, 140.74, 139.4, 139.2, 138.7, 133.5, 133.3, 133.1, 124.8, 124.4, 123.9, 120.5, 63.0, 51.4, 31.8, 30.7, 29.4, 29.3, 22.9, 17.6, 14.5, 11.9; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{55}H_{57}Cl_4NO_5S_4Si$: m/z = 1109.1619; found: m/z = 1109.1623 (δm/m = 0.62 ppm).

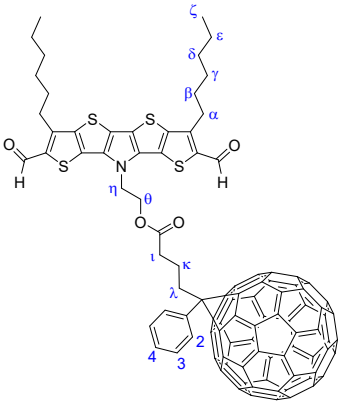


3,6-Dihexyl-9-(2-hydroxyethyl)-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]pyrrole-2,7-dicarbaldehyde ***5****.* Dialdehyde **4** (225 mg, 314 µmol) was dissolved in a mixture of THF/HCl (30%) (2:1, 30 mL) and stirred for 5.5 h at 60 °C. The mixture was poured in diethyl ether, washed two times with water and the aqueous phases were extracted to times with diethyl ether. After purification by

column chromatography over silica gel, alcohol **5** (142 mg, 253 µmol, 80.7% yield) was obtained as an orange solid, which was precipitated and filtered from methanol. Mp 213.3-216.0 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 10.04 (s, 2H, CHO), 4.54 (t, $^{3}J_{Hϑ\text{-}Hη}$ *= 5.0 Hz*, 2H, Hθ), 4.13 (t, $^{3}J_{Hη\text{-}Hϑ}$*= 5.0 Hz*, 2H, Hη), 3.10 (t, $^{3}J_{Hα\text{-}Hβ}$ *= 7.6 Hz*, 4H, Hα), 1.87-1.80 (m, 4H, Hβ), 1.68 (s, 1H, OH), 1.44-1.23 (m, 12 H, Hγ-Hε), 0.91-0.87 (m, 6H, Hζ); ^{13}C-NMR (125 MHz, $CDCl_3$): δ [ppm] = 181.8, 146.7, 141.7, 137.2, 137.1, 129.0, 122.1, 62.2, 50.9, 31.6, 30.4, 29.3, 28.1, 22.7, 14.2; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{28}H_{33}NO_3S_4$: m/z = 559.1338; found: m/z = 559.1336 (δm/m = 0.41 ppm).

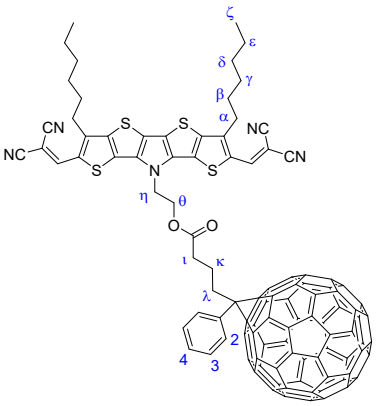


6,6-Phenyl-C_{61}-butyric acid[2-(2,7-diformyl-3,6-dihexyl-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4, 5]thieno[2,3-d]pyrrole-9-yl)ethyl]ester ***6****.* PCBA (221 mg, 205 µmol) and alcohol **5** (115 mg, 205 µmol) were dissolved in a solvent mixture of dry chlorobenzene and carbon disulfide (82 mL, 2:1) and DMAP (35.1 mg, 287 µmol) and EDC x HCl (48.8 mg, 254 µmol) were added. The mixture was treated with 3 drops of TEA and stirred at 40 °C for 5 days. The solvent was removed under reduced pressure and column chromatography over flash silica gel (DCM/EA 97:3), followed by precipitation from methanol delivered dyad **5** (254 mg, 170 µmol, 83.1% yield) as a brown solid which was precipitated and filtered from methanol. Mp (DSC, onset): 221.7 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 10.07 (s, 2H, CHO), 7.79-7.77 (m, 2H, H3), 7.49-7.40 (m, 3H, H2, H4), 4.61(t, $^{3}J_{Hϑ\text{-}Hη}$ *= 4.8 Hz*, 2H, Hθ), 4.50 (t, $^{3}J_{Hη\text{-}Hϑ}$*= 4.7 Hz*, 2H, Hη), 3.10 (t, $^{3}J_{Hα\text{-}Hβ}$ *= 7.6 Hz*, 4H, Hα), 2.67-2.63 (m, 2H, Hλ), 2.37 (t, $^{3}J_{Hι\text{-}Hκ}$ *= 6.9 Hz*, 2H, Hι), 1.98-1.91 (m, 2H, Hκ), 1.87-1.80 (m, 4H, Hβ), 1.44-1.26 (m, 12H, Hγ-Hε), 0.91-0.87 (m, 6H, Hζ). ^{13}C-NMR (125 MHz, $CDCl_3$, UDEFT): δ [ppm] = 181. 7, 172.6, 148.9, 147.8, 146.6, 145.8, 145.3, 145.3, 145.2, 145.2, 144. 9, 144.8, 144.7, 144.6, 144.4, 144.1, 143.9, 143. 8, 143.1, 143.1, 143.1, 143.0, 142.3, 142.2, 142.2, 142.2, 141.9, 140.8, 138.0, 137.6, 137.3, 137.0, 136.7, 132.1, 128.6, 128.5, 128.4, 122.6, 79.8, 63.4, 51.6, 47.5, 33. 5, 33.1, 31.7, 30.4, 29.4, 28.2, 22.7, 21.9, 14.2. HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{99}H_{43}NO_4S_4$: m/z = 1437.2023; found: m/z = 1437.2031 (δm/m = 0.56 ppm).



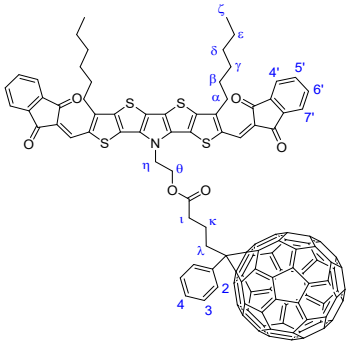
6,6-Phenyl-C_{61}-butyric acid {2-[2,7-bis(2,2-dicyanovinyl)-3,6-dihexyl-9H-thieno[2',3':4,5]thieno[3,2-b]-thieno[2',3':4,5]thieno[2,3-d]pyrrol-9-yl]ethyl} ester ***D11****.* Aldehyde **6** (21.6 mg, 15.0 µmol) and malonodinitrile (59.5 mg, 0.90 mmol) were dissolved in DCE (6 mL) and ammonium acetate (69.4 mg, 0.90 mmol) was added. The mixture was heated to 70 °C for 5 days. After cooling to room temperature, the solvent was removed under reduced pressure, the residue was dissolved in a small amount of DCM and precipitated from methanol. The remaining solid was filtered and column chromatography over

flash silica gel (first DCM followed by DCM/EA 97/3) afforded ester **D11** (18.5 mg, 12.1 µmol, 80.3% yield) as a dark solid, which appeared pink in DCM solution. **D11** was precipitated and filtered from methanol. Mp, no melting up to 360 °C (DSC); ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.91 (s, vinyl-H, 2H), 7.80-7.78 (m, 2H, H3), 7.52-7.42 (m, 3H, H2, H4), 4.68 (t, $^{3}J_{Hϑ\text{-}Hη}$ = *4.7Hz*, 2H, Hθ), 4.52 (t, $^{3}J_{Hη\text{-}Hϑ}$= *4.6 Hz*, 2H, Hη), 2.93 (t, $^{3}J_{Hα\text{-}Hβ}$ = *7.7 Hz*, 4H, Hα), 2.70-2.66 (m, 2H, Hλ), 2.44 (t, $^{3}J_{Hι\text{-}Hκ}$ = *6.9 Hz*, 2H, Hι), 2.01-1.94 (m, 2H, Hκ), 1.79-1.77 (m, 4H, Hβ), 1.43-1.25 (m, 12H, Hγ-Hε), 0.93-0.89 (m, 6H, Hζ); ^{13}C-NMR (125 MHz, UDEFT, d_2-TCE): δ [ppm] = 172.8, 149.1, 148.9, 148.1, 147.9, 145.9, 145.4, 145.3, 145.2, 145.2, 145.0, 144.8, 144.7, 144.5, 144.2, 143.9, 143.9, 143.2, 143.1, 143.1, 143.0, 142.3, 142.3, 142.2, 142.2, 141.0, 140.9, 138.0, 137.9, 137.7, 136.7, 132.2, 130.8, 129.5, 128.7, 128.6, 124.97, 115.5, 114.3, 80.0, 74.5, 51.7, 33.6, 33.2, 31.8, 30.7, 30.0, 29.6, 29.2, 22.9, 22.0, 14.5; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{105}H_{43}N_5O_2S_4$: m/z =1533.2298; found: m/z = 1533.2278 (δm/m = 1.33 ppm).



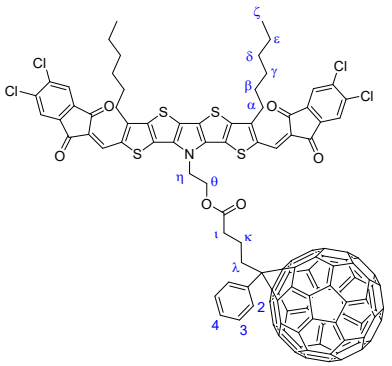
6,6-Phenyl-C_{61}-butyric acid {2-{2,7-bis[(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene) methyl]-3,6-dihexyl-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]pyrrol-9-yl} ethyl} ester ***D12***.

Dialdehyde **6** (20.00 mg, 13.90 µmol) and 1,3-indandione (8.13 mg, 55.61 µmol) were dissolved in 8 mL DCE and piperidine (13.73 µL, 139.00 µmol) was added. The mixture was stirred at room temperature for 2 d. After removing the solvent under reduced pressure, the mixture was purified via column chromatography over flash silica gel (first DCM/Et_2O 90/10, then 80/20), followed by precipitation from methanol to attain D-A-dyad **D12** (15.50 mg, 19.14 µmol, 65.8%) as a dark blue solid which was precipitated and filtered from methanol. Mp no melting up to 360 °C (DSC); ^{1}H-NMR (500 MHz, d_2-TCE, 80 °C): δ [ppm] = 8.06 (s, vinyl-H, 2H), 7.92-7.86 (m, 4H, H4', H7'), 7.71-7.68 (m, 4H, H5', H6'), 7.65-7.63 (m, 2H, H2), 7.34-7.27 (m, 3H, H3, H4), 4.82 (t, $^{3}J_{Hϑ\text{-}Hη}$ = *4.7Hz*, 2H, Hθ), 4.65 (t, $^{3}J_{Hη\text{-}Hϑ}$= *4.8 Hz*, 2H, Hη), 3.06 (t, $^{3}J_{Hα\text{-}Hβ}$ = *7.8 Hz*, 4H, Hα), 2.63-2.60 (m, 2H, Hλ), 2.43 (t, $^{3}J_{Hι\text{-}Hκ}$ = *7.1 Hz*, 2H, Hι), 1.90-1.84 (m, 2H, Hκ), 1.83-1.77 (m, 4H, Hβ), 1.37-1.23 (m, 12H, Hγ-Hε), 0.88-0.86 (m, 6H, Hζ); ^{13}C-NMR (125 MHz, UDEFT, d_2-TCE): δ [ppm] = 190.5, 190.0, 150.2, 148.8, 147.8 146.4, 146.2, 146.0, 145.7, 145.3, 145.3, 145.1, 145.1, 144.9, 144.7, 144.6, 144.3, 144.0, 143.9, 143.7, 143.3, 143.1, 143.0, 142.9, 142.2, 142.2, 142.1, 140.9, 140.7, 140.5, 138.1, 137.9, 137.6, 136.6, 135.2, 135.0, 133.0, 132.1, 131.7, 128.6, 128.3, 124.0, 123.0, 123.0, 122.3, 120.6, 99.8, 80.1, 79.9, 79.8, 79.7, 33.7, 31.8, 30.9, 30.0, 29.7, 29.4, 22.9, 14.6; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{117}H_{51}NO_6S_4$: m/z =1694.2584; found: m/z = 1694.2593 (δm/m = 0.54 ppm).

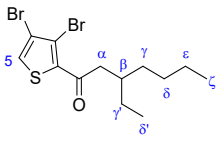


6,6-Phenyl-C_{61}-butyric acid {2-{2,7-bis[(5,6-dichloro-1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)methyl]-3,6-dihexyl-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]pyrrol-9-yl}ethyl } ester ***D13***.

Aldehyde **6** (100 mg, 69.5 µmol) and 5,6-dichloro-1H-indene-1,3(2H)-dione (59.8 mg, 278 µmol) were dissolved in chloroform (30 mL) and pyridine (0.6 mL) was added. The reaction mixture was heated to 70 °C (reflux) for two days. TLC indicated that the reaction was not finished yet and therefore 5,6-dichloro-1H-indene-1,3(2H)-dione (59.8 mg, 278 µmol) and piperidine (0.6 mL) were added once again. After another 24 hours stirring at 70 °C, the solvent was removed under reduced pressure and column chromatography over flash silica gel (DCM/ EA, 90:10) afforded **D13** (102 mg, 55.4 µmol, 79.7%) as a dark blue solid which was precipitated and filtered from methanol. Mp > 360 °C (DSC); ^{1}H-NMR (500 MHz, d_2-TCE, 80 °C): δ [ppm] = 7.86 (s, vinyl-H, 2H), 7.75 (s, 2H, IND-H) 7.61(s, 2H, IND-H), 7.53-7.51(m, 2H, H2), 7.25-7.24 (m, 3H, H3, H4), 4.75 (m, 2H Hθ), 4.54 (m, 2H, Hη), 2.90-2.87 (m, 4H, Hα), 2.45-2.42 (m, 2H, Hλ), 2.32-2.30 (m, 2H, Hι), 1.77-1.71 (m, 2H, Hκ), 1.67-1.61 (m, 4H, Hβ), 1.38-1.23 (m, 12H, Hγ-Hε), 0.84-0.81 (m, 6H, H ζ); ^{13}C-NMR (126 MHz, UDEFT, d_2-TCE): δ [ppm] = 187.6, 187.4, 173.0, 150.9, 148.7, 147.7, 145.6, 145.3, 145.3, 145.1, 145.1, 145.0, 144.9, 144.7, 145.0, 144.2, 144.0, 143.8, 143.7, 143.5, 143.1, 143.0, 143.0, 142.9, 142.9, 142.2, 142.1, 141.9, 140.8, 140.7, 139.6, 139.5, 139.2, 138.1, 137.7, 137.6, 136.5, 133.3, 133.1, 132.0, 132.0, 128.6, 128.4, 125.0, 124.5, 124.3, 121.0, 79.8, 51.5, 33.7, 31.8, 30.7, 29.7, 29.4, 22.9, 14.5; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{117}H_{47}Cl_4NO_6S_4$: m/z =1832.1046; found: m/z = 1832.1050 (δm/m = 0.21 ppm).

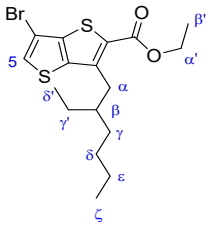


1-(3,4-Dibromothien-2-yl)-3-ethylheptan-1-one ***9***. 3,4-Dibromothiophene **7** (1.96 mL, 17.8 mmol) was dissolved under argon in dry DCM (23 mL) and cooled to 0°C in ice water. Afterwards, aluminum trichloride (5.45 g, 40.9 mmol) was added and the mixture turned red. Within 15 min, 3-ethylheptanoyl chloride (3.30 g, 86.8 mmol) was added dropwise. After stirring the reaction mixture for 4 h at 0 °C, it was poured in 0.6 M HCl (150 mL). The mixture was extracted three times with DCM and the collected organic phases were washed two times with sodium chloride solution and dried over magnesium sulfate. After evaporation of the solvent and purification by column chromatography over silica gel (first PE, then PE/DCM 4:1) acylthiophene **9** (5.67 g, 14.8 mmol, 83.5% yield) was isolated as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.59 (s, 1H, H5), 2.99-2.91 (m, 2H, Hα), 2.09-2.04 (m, 1H, Hβ), 1.44-1.28 (m, 8H, Hγ – Hζ, Hγ‘), 0.90-0.87 (m, 6H, Hδ‘, Hζ‘); ^{13}C-NMR (126 MHz, UDEFT, $CDCl_3$): δ [ppm] = 192.1, 139.9, 129.0, 117.2, 117.0, 45.8, 35.6,

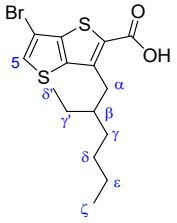


33.2, 29.0, 26.5, 23.1, 14.2, 11.0. HR-MS (FTICR-APCI): $[M]^+$ calculated for $C_{13}H_{18}Br_2OS$: m/z =380.9341; found: m/z = 380.9338 (δm/m = 0.89 ppm).

Ethyl 6-bromo-3-(2-ethylhexyl)thieno[3,2-b]thiophene-2-carboxylate ***10***. Ketone **9** (5.67 g, 14.8 mmol) was dissolved in dry DMF (29 mL) and cesium carbonate (24.2 g, 74.2 mmol) was added which turned the color of the solution from yellow to black. The solution was purged with argon and ethylmercaptoacetate (1.63 mL, 14.9 mmol) was added dropwise which changed the color to brown. The mixture was stirred for 7 d at 70 °C. After the removal of DMF in vacuum, water (200 mL) was poured into the brown reaction mixture and it was extracted 3 times with diethyl ether. Purification via column chromatography over flash silica gel (PE:DCM 1:1) delivered ester **10** (3.04 g, 7.54 mmol, 50.8%) as a yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.42 (s, 1H, H5), 4.36 (q, $^3J_{H\text{-}H}$ *= 7.1 Hz*, 2H, Hα'), 3.14-3.04 (m, 2H, Hα), 1.91-1.81 (m, 1H, Hβ), 1.39 (t, 3H, $^3J_{H\text{-}H}$ *= 7.2 Hz*, Hβ'), 1.37-1.24 (m, 8H, Hγ – Hζ, Hγ'), 0.90-0.84 (m, 6H, Hδ', Hζ');^{13}C-NMR (126 MHz, UDEFT, $CDCl_3$): δ [ppm] = 162.9, 143.6, 141.9, 140.7, 129.4, 127.5, 103.2, 61.3, 39.9, 33.6, 32.9, 28.8, 26.1, 23.2, 14.5, 14.2, 11.0. HR-MS (FTICR-APCI): $[M]^+$ calculated for $C_{17}H_{23}BrO_2S_2$: m/z =405.0375; found: m/z = 405.0385 (δm/m = 2.37 ppm).

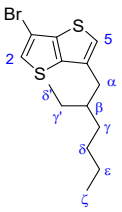


6-Bromo-3-(2-ethylhexyl)thieno[3,2-b]thiophene-2-carboxylic acid ***11***. Ester **10** (9.00 g, 22.3 mmol), lithium hydroxide (1.87 g, 44.6 mmol), THF (33 mL), methanol (5.4 mL) and water (10.8 mL) were refluxed for 23 h at 80 °C. Afterwards, the solution was slowly poured in concentrated hydrochloric acid (15 mL) and brought up to 200 mL with water. The aqueous phase was extracted three times with DCM. The solvent was removed under reduced pressure and the remaining precipitate was suspended in PE and filtered to afford carboxylic acid **11** (6.58 g, 17.5 mmol, 78.6% yield) was isolated as a white solid. Mp 108.0 °C - 110.0 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.49 (s, 1H, H5), 3.12-3.10 (m, 2H, Hα), 1.92-1.85 (m, 1H, Hβ), 1.40-1.25 (m, 8H, Hγ-Hζ, Hγ'), 0.91-0.86 (m, 6H, Hδ', Hζ'). ^{13}C-NMR (126 MHz, UDEFT, $CDCl_3$): δ [ppm] = 168.3, 145.7, 143.1, 141.0, 128.5, 128.2, 103.4, 40.2, 33.8, 33.1, 28.9, 26.3, 23.2, 14.3, 11.0. HR-MS (FTICR-APCI): $[M]^+$ calculated for $C_{15}H_{19}BrO_2S_2$: m/z =377.0062; found: m/z = 377.0064 (δm/m = 0.61 ppm).

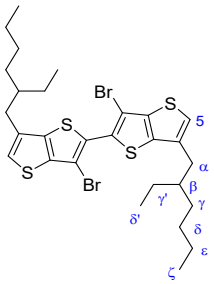


Synthesis of 3-bromo-6-(2-ethylhexyl)thieno[3,2-b]thiophene ***12***. Carboxylic acid **11** (502 mg, 1.34 mmol) and copper powder (85.0 g, 1.34 mmol) were put in quinoline (1.4 mL) and heated to 230 °C for 3.5 h until no gas formation was notable anymore. The copper powder was removed from the chilled reaction mixture and the filtrate was poured in PE. The organic phase was washed two times with 1 M HCl and one time with water and sodium chloride solution. The aqueous phases were extracted two

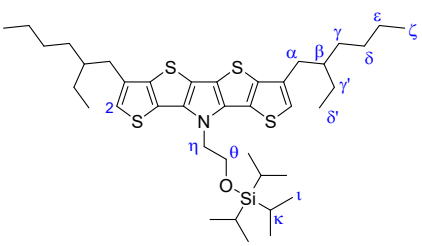
times with PE. After drying over magnesium sulfate and column chromatography over silica gel(PE), thienothiophene **12** (328 mg, 0.99 mmol, 74% yield) was isolated as colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.24 (d, 1H, H2), 7.02 (m, 1H, H5), 2.62 (d, 2H, $^{3}J_{H\text{-}H}$ *= 7.2 Hz,* Hα), 1.79-1.72 (m, 1H, Hβ), 1.36-1.25 (m, 8H, Hγ – Hζ, Hγ‘), 0.91-0.87 (m, 6H, Hδ‘, Hζ‘); ^{13}C-NMR (126 MHz, UDEFT, $CDCl_3$): δ [ppm] = 140.0, 139.5, 135.2, 123.6, 123.5, 103.1, 38.9, 34.3, 32.8, 29.0, 26.0, 23.2, 14.3, 10.9; HR-MS (FTICR-APCI): $[M]^+$ calculated for $C_{14}H_{19}BrS_2$: m/z =333.0163; found: m/z = 333.0174 (δm/m = 3.27 ppm).



3,3'-Dibromo-6,6'-bis(2-ethylhexyl)-2,2'-bithieno[3,2-b]thiophene ***13****.* Diisopropylamine (1.62 mL, 11.5 mmol) was poured in with argon purged, dry THF (30 mL) and cooled to 0 °C. Within 15 min, *n*-BuLi (7.16 mL, 11.5 mmol, 1.6 M in hexane) was added dropwise. The solution was stirred for 15 min until thienothiophene **12** (3.80 g, 11.5 mmol) was added and the solution changed its color to orange. The mixture was stirred for 1.5 h at 0 °C before copper (II) chloride (1.54 g, 11.5 mmol) was added and the mixture was stirred for 23 h at 0 °C up to r.t. The reaction mixture was poured in water (200 mL) and the aqueous phase was extracted three times with PE. The organic phases were collected and washed four times with water and dried over magnesium sulfate. Column chromatography over silica gel (PE) delivered bithienothiophene **13** (2.35 g, 3.56 mmol, 62.2% yield) as light yellow oil that crystallizes in the fridge. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.08 (s, 2H, H5), 2.65 (d, 4H, $^{3}J_{H\text{-}H}$ *= 7.1 Hz,* Hα), 1.80-1.74 (m, 2H, Hβ), 1.38-1.26 (m, 16H, Hγ-Hζ, Hγ‘), 0.92-0.87 (m, 12H, Hδ‘, Hζ‘); ^{13}C-NMR (100 MHz, $CDCl_3$): δ [ppm] = 140.6, 139.4, 135.2, 129.9, 123.8, 105.7, 39.0, 34.3, 32.8, 29.0, 26.0, 23.1, 14.3, 11.0; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{28}H_{36}Br_2S_4$: m/z = 660.0041; found: m/z = 660.0022 (δm/m = 2.88 ppm).

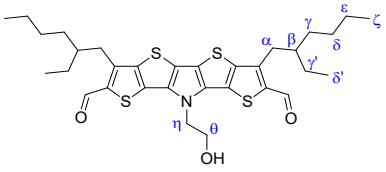


3,6-Bis(2-ethylhexyl)-9-{2-[(triisopropylsilyl)oxy]ethyl}-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4, 5]thieno[2,3-d]pyrrole ***14****.* Bithienothiophene **13** (52.1 mg, 79.9 µmol), $Pd(dba)_2$ (4.53 mg, 7.89 µmol), dppf (17.5 mg, 31.5 µmol) and NaO^tBu (75.8 mg, 0.79 mmol) were dissolved in with argon purged, dry toluene (1.3 mL). The mixture was purged again with argon for 30 min until 2-[(triisopropylsilyl)oxy]-ethan-1-amine (21.4 µL, 94.6 µmol) was added and the mixture was purged again. The mixture was stirred for 20 h at 110 °C. Afterwards, the solvent was removed and column chromatography over silica gel (DCM/PE 1:4) delivered SN5'-derivative **14** (50.9 mg, 75.4 µmol, 95.6% yield) as a light yellow oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 6.85 (s, 2H, H2), 4.50 (t, $^{3}J_{H\eta\text{-}H\vartheta}$*= 6.0 Hz*, 2H, Hη), 4.14 (t, $^{3}J_{H\vartheta\text{-}H\eta}$ *= 6.0 Hz*, 2H, Hθ), 2.66 (d, $^{3}J_{H\alpha\text{-}H\beta}$ *= 7.2 Hz*, 4H, Hα), 1.87-1.83 (m, 1H, Hβ), 1.39-1.30 (m, 16 H, Hγ-Hε, Hγ‘), 0.94- 0.83 (m, 33H,

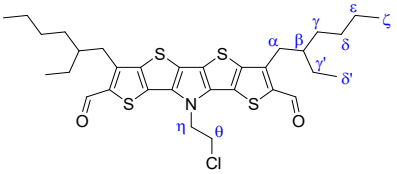


Hζ, Hζ‘, Hκ, Hι); ^{13}C-NMR (400 MHz, $CDCl_3$): δ [ppm] = 139.2, 135.6, 135.3, 123.1, 118.8, 117.3, 63.1, 50.4, 38.8, 34.0, 32.8, 28.9, 25.9, 23.0, 17.6, 14.2, 11.8, 10.9; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{39}H_{61}NOS_4Si$: m/z = 715.3400; found: m/z = 715.3395 (δm/m = 0.62 ppm).

3,6-Bis(2-ethylhexyl)-9-(2-hydroxyethyl)-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]-pyrrole-2,7-dicarbaldehyde ***15****.* DMF (27.0 µL, 0.35 mmol) were dissolved in dry DCM (1 mL) and phosphoryl chloride (13.7 µL, 0.15 mmol) was added. After stirring for 1 h at r.t, heteroacene **14**, dissolved in dry DCM (6 mL) was added, and the mixture turned red. The red solution was heated to reflux overnight which leads to volatilization of the solvent. DCM, and aqueous sodium hydroxide solution were added to the residue and the two-phase system was stirred vigorously for 1 d. After separation of the two phases and aqueous work-up of the organic layer, column chromatography over flash silica gel (from DCM: Et_2O 5% to DCM: Et_2O 5%: EA 15%) delivered chlorinated SN5' **16** (26.55 mg, 41.95 µmol, 60.1%) and alcohol 1**5** (17.13 mg, 27.85 µmol, 39.9%) as yellow solids. Mp 194.7 – 196.3 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 10.01 (s, 2H, CHO), 4.54 (t, $^3J_{Hη\text{-}Hϑ}$*= 4.9 Hz*, 2H, Hη), 4.14 (t, $^3J_{Hϑ\text{-}Hη}$ *= 4.5 Hz*, 2H, Hθ), 3.00 (d, $^3J_{Hα\text{-}Hβ}$ *= 7.4 Hz*, 4H, Hα), 1.92-1.86 (m, 2H, Hβ), 1.41-1.25 (m, 16 H, Hγ-Hε, Hγ‘), 0.96-0.86 (m, 12H, Hζ, Hζ‘); ^{13}C-NMR (101 MHz, $CDCl_3$, UDEFT): δ [ppm] = 181.9, 146.2, 141.9, 137.9, 137.0, 128.9, 122.2, 62.2, 50.9, 40.8, 33.1, 32.7, 29.0, 26.3, 23.1, 14.2, 11.0; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{32}H_{41}NO_3S_4$: m/z = 615.1964; found: m/z = 615.1962 (δm/m = 0.33 ppm).

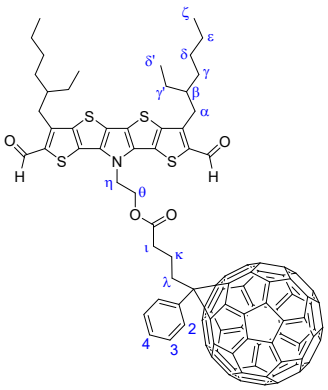


9-(2-Chloroethyl)-3,6-bis(2-ethylhexyl)-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]-pyrrole-2,7-dicarbaldehyde ***16****.* ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 10.05 (s, 2H, CHO), 4.73 (t, $^3J_{Hη\text{-}Hϑ}$ *= 5.8 Hz*, 2H, Hη), 3.99 (t, $^3J_{Hϑ\text{-}Hη}$ *= 5.8 Hz*, 2H, Hθ), 3.02 (d, $^3J_{Hα\text{-}Hβ}$ *= 7.4 Hz*, 4H, Hα), 1.93-1.85 (m, 2H, Hβ), 1.44-1.26 (m, 16 H, Hγ-Hε, Hγ‘), 0.96-0.87 (m, 12H, Hζ, Hζ‘); ^{13}C-NMR (125 MHz, $CDCl_3$, UDEFT): δ [ppm] = 181.9, 146.2, 142.1, 138.0, 136.7, 128.4, 122.6, 50.0, 43.1, 40.8, 33.1, 32.8, 29.0, 26.3, 23.1, 14.2, 11.0; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{32}H_{40}ClNO_2S_4$: m/z = 633.1625; found: m/z = 633.1620 (δm/m = 0.73 ppm).

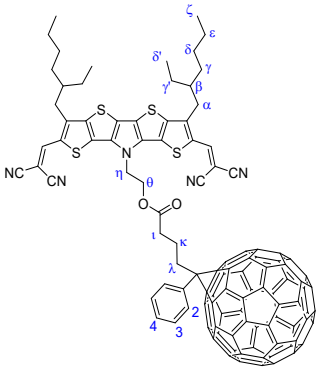


6,6-Phenyl-C$_{61}$-butyric acid {2-[3,6-bis(2-ethylhexyl)-2,7-diformyl-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]pyrrol-9-yl]ethyl} ester ***17****.* PCBA (43.5 mg, 48.5 µmol) and alcohol **15** (24.9 mg, 40.4 µmol) were dissolved in a solvent mixture of dry chlorobenzene and carbon disulfide (17 mL, 2:1) and DMAP (6.91 mg, 56.6 µmol) and EDC x HCl (9.61 mg, 50.1 µmol) were added. The mixture was

stirred at 40 °C for 7 days until the solvent was removed under reduced pressure. Purification over column chromatography (flash, DCM: Et_2O 5%) and SEC (DCM) delivered dyad **17** (35.4 mg, 23.7 µmol, 58.6%) as a brown solid which was precipitated from methanol. Mp/decomp. 214.8-219.1°C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 10.05 (s, 2H, CHO), 7.78-7.76 (m, 2H, H2), 7.48-7.41 (m, 3H, H3, H4), 4.62 – 4.60 (m, 2H, Hη), 4.51-4.48 (m, 2H, Hθ), 3.03-2.97 (m, 4H, Hα), 2.66-2.62 (m, 2H, Hλ), 2.33 (t, $^3J_{Hι\text{-}Hκ}$ *= 6.9 Hz*, 2H, Hι), 1.98-1.85 (m, 4H, Hκ, Hβ), 1.42-1.25 (m, 16H, Hγ', Hε-Hγ), 0.94-0.87 (m, 12H, Hζ, Hδ'); ^{13}C-NMR (101 MHz, $CDCl_3$, UDEFT): δ [ppm] = 181.8, 172.5, 148.9, 147.8, 146.2, 145.8, 145.2, 145.2, 145.1, 145.1, 144.8, 144.8, 144.7, 144.7, 144.6, 144.4, 144.1, 143.8, 143.8, 143.0, 142.9, 142.2, 142.2, 142.1, 140.9, 140.8, 138.0, 138.0, 137.6, 136.9, 136.7, 132.1, 128.5, 128.5, 128.3, 122.6, 79.8, 63.3, 51.6, 47.5, 40.7, 33.4, 33.1, 32.7, 29.8, 29.0, 26.3, 23.1, 21.8, 14.3, 11.1; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{103}H_{51}NO_4S_4$: m/z = 1494.2728; found: m/z = 1494.2731 (δm/m = 0.19 ppm).

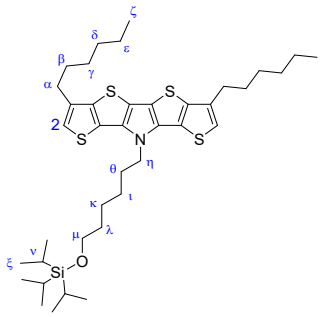


6,6-Phenyl-C_{61}-butyric acid {2-[2,7-bis(2,2-dicyanovinyl)-3,6-bis(2-ethylhexyl)-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]pyrrol-9-yl]ethyl} ester ***D14***. Dialdehyde **17** (35.5 mg, 23.8 µmol), malononitrile (94.1 mg, 1.42 mmol) and ammonium acetate (110 mg, 1.42 mmol) were dissolved in DCE (12.5 mL) and the mixture was stirred at 80 °C for 22 h. After removal of the solvent and purification over column chromatography (flash, DCM: Et_2O 3%), the desired dyad **D14** (21.9 mg, 13.8 µmol, 58.0%) was precipitated from methanol and obtained as dark solid which appears pink in DCM solution. Mp >360 °C (DSC); ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.88 (s, 2H, vinyl-H), 7.80-7.78 (m, 2H, H2), 7.52-7.44 (m, 3H, H3, H4), 4.69-4.67 (m, 2H, H Hη), 4.54-4.52 (m, 2H, Hθ), 2.86-2.82 (m, 4H, Hα), 2.70-2.66 (m, 2H, Hλ), 2.41 (t, $^3J_{Hι\text{-}Hκ}$ *= 7.0 Hz*, 2H, Hι), 2.01-1.94 (m, 2H, Hκ), 1.85-1.77 (m, 2H, Hβ), 1.41-1.24 (m, 16H, Hγ', Hγ-Hε), 0.95-0.89 (m, 12H, Hζ, Hδ'); ^{13}C-NMR (101 MHz, $CDCl_3$, UDEFT): δ [ppm] = 172.4, 148.8, 148.2, 148.0, 147.8, 145.8, 145.3, 145.2, 145.1, 145.1, 144.9, 144.8, 144.7, 144.6, 144.4, 144.1, 143.9, 143.8, 143.2, 143.1, 143.0, 142.9, 142.3, 142.2, 142.1, 142.1, 141.0, 140.8, 138.0, 137.7, 137.6, 136.7, 132.1, 131.3, 129.1, 128.6, 128.4, 124.5, 115.0, 114.0, 79.8, 74.3, 63.3, 51.6, 48.0, 41.1, 33.6, 33.3, 33.2, 33.1, 28.9, 26.4, 23.1, 21.8, 14.3, 11.1; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{109}H_{51}N_5O_2S_4$: m/z = 1590.2952; found: m/z = 1590.2950 (δm/m = 0.12 ppm).

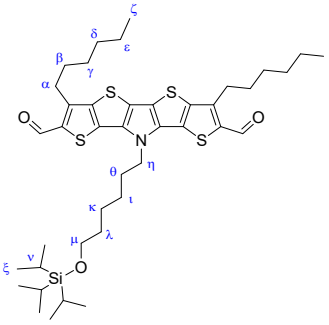


3,6-Dihexyl-9-(6-((triisopropylsilyl)oxy)hexyl)-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno-[2,3-d]pyrrole ***19***. 3,3'-Dibromo-6,6'-bis(2-ethylhexyl)-2,2'-bithieno[3,2-b]thiophene **1** (51.6 mg, 0.85

µmol), $Pd(dba)_2$ (4.91 mg, 8.54 µmol), dppf (18.9 mg, 34.1 µmol), and NaO^tBu (82.0 mg, 0.85 mmol) were dissolved in argon purged, dry toluene (1.4 mL). The mixture was purged again with argon for 30 min until 2-[(triisopropylsilyl)oxy]hexan-1-amine (23.9 µL, 93.9 µmol) was added and the mixture was purged again. The mixture was stirred for 23 h at 110 °C. Afterwards, the solvent was removed and column chromatography over silica gel (DCM/PE 1:4) delivered SN5'-derivative **19** (59.6 mg, 83.2 µmol, 97.5% yield) as a light yellow solid. Mp 30.0-31.9 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 6.88 (s, 2H, H2), 4.37 (t, $^3J_{Hη-Hϑ}$= *7.1 Hz*, 2H, Hη), 3.62 (t, $^3J_{Hμ-Hλ}$= *6.4 Hz*, 2H, Hμ), 2.74 (t, $^3J_{Hα-Hβ}$ = *7.7 Hz*, 4H, Hα) 2.02-1.95 (m, 2H, Hθ), 1.83-1.75 (m, 4H, Hβ), 1.52v 1.32 (m, 18H, Hγ-Hε, Hι-Hλ), 1.04v 1.00 (m, 21H, Hξ, Hν), 0.92v 0.88 (m, 6H, Hζ). ^{13}C-NMR (400 MHz, $CDCl_3$): δ [ppm] = 139.0, 136.8, 135.1, 123.1, 123.0, 118.1, 117.1, 63.3, 54.7, 48.6, 32.8, 31.8, 29.6, 29.3, 28.9, 26.8, 25.7, 22.8, 18.2, 14.3, 12.1; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{39}H_{61}NOS_4Si$: m/z = 715.3400; found: m/z = 715.3393 (δm/m = 1.01 ppm).

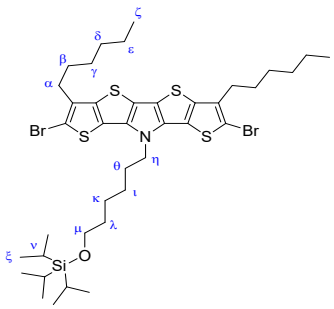


3,6-Dihexyl-9-{6-[(triisopropylsilyl)oxy]hexyl}-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno-[2,3-d]pyrrole-2,7-dicarbaldehyde ***20****.* Heteroacene **19** (30.0 mg, 34.3 µmol) was dissolved in purged, dry THF (1 mL) and cooled to -78 °C. Afterwards, *n*-BuLi (1.6 M in hexane, 0.05 mL, 0.09 mmol) was added dropwise within 10 min. The mixture was stirred for 1.5 h at -78 °C and then quenched with N-formylpiperidine (15 µL, 0.14 mmol). After the solution was stirred for 18 h and thawed to r.t., water was added and the mixture was extracted three times with diethyl ether. The organic phases were dried over magnesium sulfate and column chromatography over flash silica gel (DCM, 1% EA) delivered dialdehyde **20** (13.0 mg, 0.02 mmol, 49.0% yield) as a yellow solid. Mp 150.5-151.9 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 10.08 (s, 2H, CHO), 4.41 (t, $^3J_{Hη-Hϑ}$= *7.1 Hz*, 2H, Hη), 3.60 (t, $^3J_{Hμ-Hλ}$= *6.4 Hz*, 2H, Hμ), 3.12 (t, $^3J_{Hα-Hβ}$ = *7.7 Hz*, 4H, Hα), 2.02-1.95 (m, 2H, Hθ), 1.98-1.81 (m, 4H, Hβ), 1.51-1.25 (m, 18H, Hγ-Hε, Hι-Hλ), 1.05-0.97 (m, 21H, Hξ, Hν), 0.91-0.88 (m, 6H, Hζ); ^{13}C-NMR (125 MHz, $CDCl_3$, UDEFT): δ [ppm] = 181.7, 146.7, 141.5, 137.1, 136.7, 128.8, 121.7, 63.2, 48.9, 32.8, 31.8, 31.6, 30.4, 29.3, 28.1, 26.9, 25.7, 22.7, 18.2, 14.2, 12.1. HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{41}H_{61}NO_3S_4Si$: m/z = 771.3298; found: m/z = 771.3300 (δm/m = 0.18 ppm).

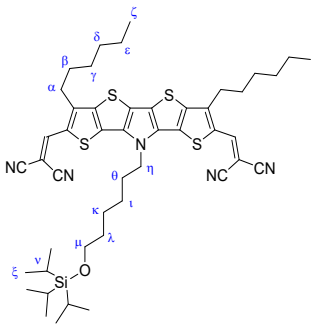


2,7-Dibromo-3,6-dihexyl-9-{6-[(triisopropylsilyl)oxy]hexyl}-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2', 3':4,5]thieno[2,3-d]pyrrole ***21****.* Brominated heteroacene **19** (491 mg, 686 µmol) was dissolved in chloroform (22 mL) cooled in an ice bath to 0 °C under light-exclusion. NBS (269 mg, 1.51 mmol) was added

to the reaction mixture and after 10 minutes of stirring at 0 °C, the ice bath was removed and the mixture thawed to r.t. After stirring for 3 h, the organic phase was washed two times with sodium disulfite and one time with sodium chloride solution. The aqueous phases were collected and extracted three times with DCM. Purification via column chromatography over flash silica gel (PE:DCM 4:1) delivered bromide **21** (485 mg, 0.56 mmol, 81%) as a beige solid. Mp 71.6-72.9 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 4.24 (t, $^{3}J_{Hη\text{-}Hϑ}$= *6.9 Hz*, 2H, Hη), 3.62 (t, $^{3}J_{Hμ\text{-}Hλ}$= *6.4 Hz*, 2H, Hμ), 2.74 (t, $^{3}J_{Hα\text{-}Hβ}$ = *7.6 Hz*, 4H, Hα), 1.97-1.89 (m, 2H, Hθ), 1.77-1.69 (m, 4H, Hβ), 1.52v 1.32 (m, 18H, Hγ-Hε, Hι-Hλ), 1.04v 1.01 (m, 21H, Hξ, Hν), 0.91v 0.88 (m, 6H, Hζ); ^{13}C-NMR (125 MHz, $CDCl_3$, UDEFT): δ [ppm] = 137.2, 135.8, 135.1, 121.5, 116.4, 106.4, 63.2, 48.7, 32.7, 31.8, 31.7, 29.2, 29.0, 28.3, 26.8, 25.6, 22.7, 18.2, 14.2, 12.1; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{39}H_{59}Br_2NOS_4Si$: m/z = 873.1592; found: m/z = 873.1603 (δm/m = 1.23 ppm).

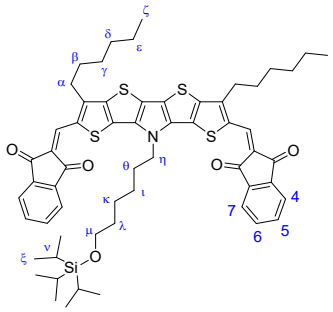


2,2'-{{3,6-Dihexyl-9-{2-[(triisopropylsilyl)oxy]hexyl}-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]-thieno[2,3-d]pyrrole-2,7-diyl}bis(methaneylylidene)} dimalononitrile ***R15***. Dialdehyde **20** (30.0 mg, 38.9 µmol), malononitrile (103 mg, 1.55 mmol) and ammonium acetate (120 mg, 1.55 mmol) were dissolved in DCE (6 mL) and the mixture was stirred at 80 °C for 17 h. TLC revealed formation of a side product or incomplete conversion. Therefore, the same amount of malononitrile and ammonium acetate was added again and stirred for 4 days at 80 °C. After removal of the solvent and purification over column chromatography (DCM:Et_2O 2%), the received product was precipitated from methanol. The mass spectrum revealed that one part of TIPS-protecting group was cleaved off in a small amount of product which was not possible to separate. **R15** was obtained as a greenish solid (20.0 mg, 23.0 µmol, 59.3%) with pink color in DCM solution. Mp 298.1-300.4 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.89 (s, 2H, vinyl-H), 4.40 (t, $^{3}J_{Hη\text{-}Hϑ}$ = *6.6 Hz*, 2H, Hη), 3.60-3.56 (m, 2H, Hμ), 2.95v 2.91 (m, 4H, Hα), 2.01-1.98 (m, 2H, Hθ), 1.80-1.73 (m, 4H, Hβ), 1.46v 1.25 (m, 18H, Hγ-Hε, Hι-Hλ), 1.02v 0.89 (m, 27H, Hξ, Hν, Hζ); ^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 148.6, 147.7, 142.6, 137.6, 130.7, 129.5, 123.7, 115.2, 114.0, 111.3, 73.9, 63.2, 32.7, 31.6, 30.6, 29.4, 29.0, 26.8, 25.6, 22.6, 18.1, 14.2, 12.1; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{47}H_{61}N_5OS_4Si$: m/z = 867.3523; found: m/z = 867.3520 (δm/m = 0.30 ppm).

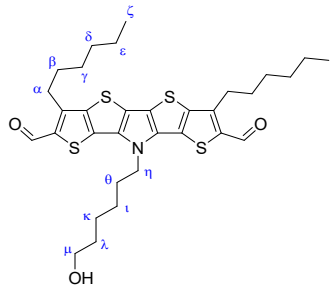


2,2'-((3,6-Dihexyl-9-(6-((triisopropylsilyl)oxy)hexyl)-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]-thieno[2,3-d]pyrrole-2,7-diyl)bis(methaneylylidene))bis(1H-indene-1,3(2H)-dione) ***R16***. Dialdehyde **20**

(20.2 mg, 16.2 µmol), IND (15.3 mg, 105 µmol) and two drops of piperidine were dissolved in DCE (3 mL) and stirred at r.t for 48 h. Afterwards, the solvent was removed under reduced pressure and column chromatography over flash silica gel (DCM: Et_2O 5%) delivered **R16** as a dark blue solid (23.4 mg, 22.8 µmol, 87%) which was precipitated and filtered from methanol. Mp 279.9-282.9 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.88 (d, $^3J_{H4\text{-}H5}$ *= 7.2 Hz,* 2H, H4), 7.84 (d, $^3J_{H7\text{-}H6}$ *= 7.3 Hz,* 2H, H7), 7.75 (s, 2H, vinyl-H), 7.60-7.57 (m, 2H, H5), 7.55v 7.52 (m, 2H, H6), 4.61 (t, $^3J_{H\eta\text{-}H\vartheta}$ *= 6.4 Hz*, 2H, Hη), 3.52 (t, $^3J_{H\mu\text{-}H\lambda}$*= 6.5 Hz*, 2H, Hμ), 3.01 (t, $^3J_{H\alpha\text{-}H\beta}$ *= 7.8 Hz*, 4H, Hα), 2.13v 2.08 (m, 2H, Hθ), 1.80-1.74 (m, 4H, Hβ), 1.47v 1.32 (m, 18H, Hγ-Hε, Hι-Hλ), 0.92-0.86 (m, 27H, Hξ, Hν, Hζ). ^{13}C-NMR (125 MHz, $CDCl_3$, UDEFT): δ [ppm] = 190.1, 189.6, 149.8, 142.8, 142.0, 140.4, 137.8, 134.6, 134.4, 132.9, 132.6, 131.7, 122.8, 122.7, 122.6, 121.6, 63.3, 49.4, 32.8, 31.7, 31.6, 30.6, 29.5, 29.2, 26.8, 25.7, 22.7, 18.1, 14.2, 12.0; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{59}H_{69}NO_5S_4Si$: m/z = 1027.3822; found: m/z = 1027.3812 (δm/m = 1.04 ppm).

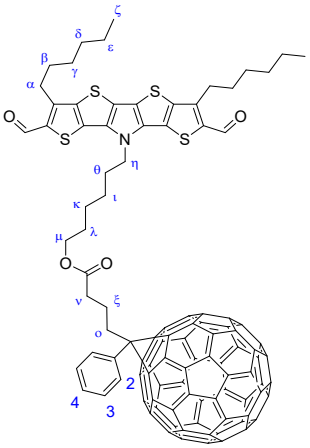


3,6-Dihexyl-9-(6-hydroxyhexyl)-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]pyrrole-2,7-dicarbaldehyde ***22****.* Dialdehyde **20** (19.7 mg, 25.5 µmol) was dissolved in a mixture of THF/HCl (30%) (2:1, 3 mL) and stirred for 3 h at 70 °C. The mixture was poured in diethyl ether, washed three times with water and the aqueous phases were extracted three times with diethyl ether. The solvent was removed under reduced pressure. After purification by column chromatography over flash silica gel, alcohol **22** (8.5 mg, 13.8 µmol, 54.1% yield) was obtained as an orange solid. Mp 163.4-166.5 °C; ^{1}H-NMR (400 MHz, CDCl3): δ [ppm] = 10.07 (s, 2H, CHO), 4.40 (t, $^3J_{H\eta\text{-}H\vartheta}$*= 7.1 Hz*, 2H, Hη), 3.60 (t, $^3J_{H\mu\text{-}H\lambda}$*= 6.5 Hz*, 2H, Hμ), 3.11 (t, $^3J_{H\alpha\text{-}H\beta}$ *= 7.7 Hz*, 4H, Hα), 2.02-1.96 (m, 2H, Hθ), 1.88-1.82 (m, 4H, Hβ), 1.71-1.25 (m, 18H, Hγ-Hε, Hι-Hλ), 0.91-0.88 (m, 6H, Hζ); ^{13}C-NMR (125 MHz, $CDCl_3$, UDEFT): δ [ppm] = 181.8, 146.8, 141.6, 137.2, 136.8, 128.8, 121.8, 62.8, 48.8, 32.6, 31.7, 31.6, 30.4, 29.3, 28.2, 26.8, 25.5, 22.7, 14.2; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{32}H_{41}NO_3S_4$: m/z = 615.1964; found: m/z = 615.1965 (δm/m = 0.20 ppm).

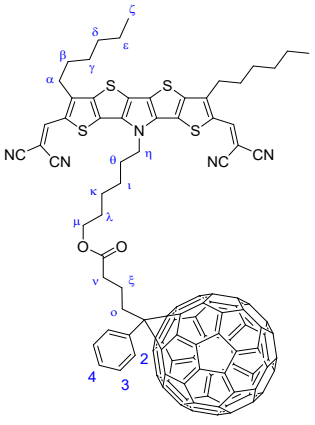


6,6-Phenyl-C_{61}-butyric acid[2-(2,7-diformyl-3,6-dihexyl-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]pyrrole-9-yl)hexyl]ester ***23***. PCBA (43.5 mg, 48.5 µmol) and alcohol **22** (24.9 mg, 40.4 µmol) were dissolved in a solvent mixture of dry chlorobenzene and carbon disulfide (18 mL, 2:1) and DMAP (6.91 mg, 56.6 µmol) and EDCxHCl (9.61 mg, 50.1 µmol) were added. The mixture was treated with some drops of TEA and stirred at 40 °C for 4 days. The solvent was removed under reduced pressure and column chromatography over flash silica gel (DCM:t_2O 7%), followed by precipitation from

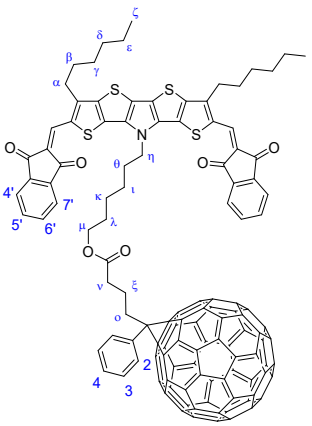
methanol delivered dyad **23** (27.6 mg, 18.5 µmol, 45.7% yield) as a brown solid. Mp 132.5-135.2 °C; ^{1}H-NMR (500 MHz, $CDCl_3$): δ [ppm] = 10.07 (s, 2H, CHO), 7.89 – 7.87 (m, 2H, H2), 7.52 – 7.49 (m, 2H, H3), 7.45-7.42 (m, 1H, H4), 4.35 (t, $^{3}J_{Hη\text{-}Hϑ}$= *7.4 Hz*, 2H, Hη), 4.06 (t, $^{3}J_{Hμ\text{-}Hλ}$= *6.4 Hz*, 2H, Hμ), 3.10 (t, $^{3}J_{Hα\text{-}Hβ}$ = *7.7 Hz*, 4H, Hα), 2.89-2.86 (m, 2H, Ho), 2.50 (t, $^{3}J_{Hν\text{-}Hξ}$= *7.3 Hz*, 2H, Hν), 2.18-2.12 (m, 2H, Hξ), 2.00-1.94 (m, 2H, Hθ), 1.87-1.81 (m, 4H, Hβ), 1.65-1.59 (m, 2H, Hλ), 1.52-1.30 (m, 16H, Hγ-Hε, Hι-Hκ), 0.91-0.88 (m, 6H, Hζ); ^{13}C-NMR (125 MHz, $CDCl_3$, UDEFT): δ [ppm] = 181.7, 173.2, 148.9, 147.9, 146.8, 145.8, 145.3, 145.2, 145.1, 145.1, 144.9, 144.8, 144.7, 144.6, 144.4, 144.1, 143.8, 143.7, 143.1, 143.0, 143.0, 142.9, 142.9, 142.3, 142.2, 142.1, 141.7, 140.9, 140.8, 138.1, 137.6, 137.2, 136.9, 136.8, 132.2, 128.8, 128.6, 128.4, 122.0, 80.0, 64.6, 52.0, 48.8, 34.3, 33.8, 31.8, 31.7, 30.4, 29.4, 28.6, 28.2, 26.8, 26.0, 22.7, 22.6, 14.3; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{103}H_{51}NO_4S_4$: m/z = 1494.2728; found: m/z = 1494.2705 (δm/m = 1.51 ppm).



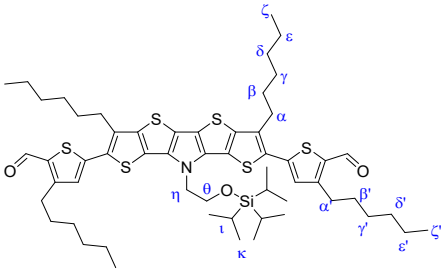
6,6-Phenyl-C_{61}-butyric acid {6-[2,7-bis(2,2-dicyanovinyl)-3,6-dihexyl-9H-thieno[2',3':4,5]thieno[3,2-b]-thieno[2',3':4,5]thieno[2,3-d]pyrrol-9-yl]hexyl} ester ***D15***. Dialdehyde **23** (30.0 mg, 20.1 µmol), malononitrile (79.6 mg, 1.20 mmol) and ammonium acetate (92.8 mg, 1.20 mmol) were dissolved in DCE (8 mL) and the mixture was stirred at 80 °C for 6 d. After removal of the solvent and purification over column chromatography (silica gel, DCM:Et_2O 3%), desired **D15** (18.1 mg, 11.4 µmol, 56.7%) was precipitated from methanol and obtained as dark solid which appears pink in DCM solution. Mp 229.4 (DSC onset); ^{1}H-NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.90-7.87 (m, 4H, vinyl-H, H2), 7.54-7.50 (m, 2H, H3), 7.47-7.43 (m, 1H, H4), 4.39 (t, $^{3}J_{Hη\text{-}Hϑ}$= *7.1 Hz*, 2H, Hη), 4.04 (t, $^{3}J_{Hμ\text{-}Hλ}$= *6.4 Hz*, 2H, Hμ), 2.94-2.86 (m, 6H, Hα, Ho) 2.48 (t, $^{3}J_{Hν\text{-}Hξ}$= *7.1 Hz*, 2H, Hν), 2.19-2.11 (m, 2H, Hθ), 2.03-1.97 (m, 2H, Hξ), 1.79-1.72 (m, 4H, Hβ), 1.64-1.58 (m, 2H, Hλ), 1.46-1.25 (m, 16H, Hγ-Hε, Hι-Hκ), 0.93-0.89 (m, 6H, Hζ); ^{13}C-NMR (101 MHz, $CDCl_3$): δ [ppm] = 173.2, 148.9,148.7, 147.9, 147.7, 145.9, 145.3, 145.2, 145.1, 145.1, 144.9, 144.8, 144.7, 144.7, 144.7, 144.6, 144.4, 144.1, 143.9, 143.7, 143.1, 143.1, 143.0, 142.9, 142.9, 142.8, 142.3, 142.2, 142.1, 140.9, 140.8, 138.1, 137.7, 137.5, 136.8, 132.2, 130.7, 129.4, 128.6, 128.4, 123.9, 115.2, 114.1, 80.0, 74.0, 64.6, 52.1, 49.1, 34.2, 33.7, 31.6, 30.5, 29.5, 29.0, 28.6, 26.8, 26.0, 22.7, 22.6, 14.2; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{109}H_{51}N_5O_2S_4$: m/z = 1590.2952; found: m/z = 1590.2930 (δm/m = 1.37 ppm).



6,6-Phenyl-C_{61}-butyric acid {2-{2,7-bis[(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene) methyl]-3,6-dihexyl-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]pyrrol-9-yl} hexyl} ester ***D16***. Dialdehyde **23** (22.00 mg, 14.72 µmol) and 1,3-indandione (8.60 mg, 58.87 µmol) and piperidine (8.7 µL, 88.31µmol) were dissolved in DCE (2 mL) and stirred for 48 h. After removal of the solvent under reduced pressure and precipitation from methanol, the mixture was purified via column chromatography over flash silica gel (DCM:Et_2O 10%) to obtain **D16** as a blue solid (10.59 mg, 6.05 µmol, 41.1%) which was precipitated and filtered from methanol. Mp > 360 °C (DSC); ^{1}H-NMR (500 MHz, $CDCl_3$): δ [ppm] = 7.89-7.76 (m, 8H, H4', H7', vinyl-H, H2), 7.62-7.54 (m, 4H, H5', H6'), 7.42-7.32 (m, 3H, H3, H4), 4.57-4.56 (m, 2H, Hη), 4.07-4.04 (m, 2H, Hµ), 3.02-2.98 (m, 4H, Hα), 2.80-2.76 (m, 2H, Ho), 2.41-2.38 (m, 2H, Hν), 2.12-2.02 (m, 4H, Hξ, Hθ), 1.76-1.72 (m, 4H, Hβ), 1.63-1.26 (m, 18H, Hλ, Hγ-Hε, Hι-Hκ), 0.92-0.89 (m, 6H, Hζ); ^{13}C-NMR (125 MHz, $CDCl_3$, UDEFT): δ [ppm] = 190.1, 189.7, 173.2, 149.9, 148.8, 147.8, 145.7, 145.3, 145.2, 145.1, 145.0, 144.8, 144.7, 144.7, 144.6, 144.3, 144.0, 143.8, 143.7, 143.0, 143.0, 143.0, 142.9, 142.9, 142.8, 142.2, 142.1, 142.1, 142.0, 140.9, 140.7, 140.4, 138.0, 137.6, 136.8, 134.7, 134.5, 132.9, 132.7, 132.1, 131.6, 128.5, 128.3, 123.0, 122.8, 122.7, 121.0, 79.9, 64.9, 51.9, 49.2, 34.3, 33.7, 31.7, 30.6, 29.5, 29.2, 28.6, 26.8, 26.2, 22.7, 22.6, 14.3; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{121}H_{59}NO_6S_4$: m/z = 1750.3252; found: m/z = 1750.3225 (δm/m = 1.58 ppm).

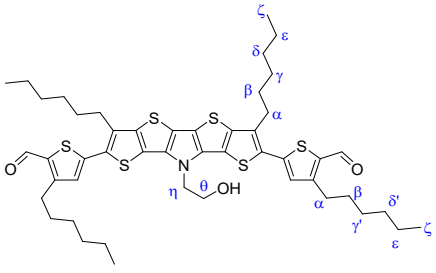


5,5'-{3,6-Dihexyl-9-[2-((triisopropylsilyl)oxy)ethyl]-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]pyrrole-2,7-diyl}bis(3-hexylthiophene-2-carbaldehyde) ***25***.

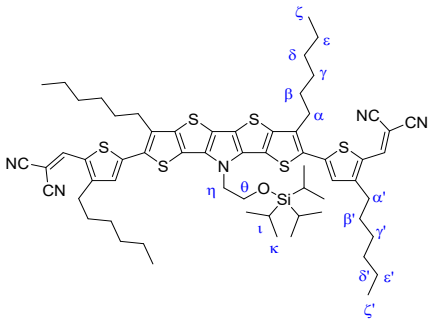


Heteroacene **3** (40.0 mg, 60.6 µmol), thiophene **24** (68.3 mg, 212 µmol) and potassium acetate (17.8 mg, 0.18 mmol) were put into a reaction flask and set under vacuum. Meanwhile, the catalyst $Pd(OAc)_2$ (0.27 mg, 1.21 µmol) was dissolved in dry, argon degassed DMF (2 mL) and degassed again for 20 minutes. DMF (2 mL) and catalyst (0.27 mg, 1.21 µmol) were added to the solid mixture and stirred at 70 °C for 2 h. Afterwards, the same amount of catalyst and solvent were added again (0.27 mg $Pd(OAc)_2$ in 2 mL DMF) and the mixture was stirred at 90 °C for 15 h. After cooling to r.t, methanol was added to the reaction mixture and the red precipitate was filtered. The red solid was purified via column chromatography (flash silica gel, DCM:Et_2O 5%) and size exclusion chromatography (DCM). Purification delivered deprotected alcohol **26** (2.8 mg, 3.1 µmol, 5.2%) and pure monomer **24** (43.9 mg, 41.9 µmol, 69.1%) as a red solid. Mp 130.4-131.9 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 9.99 (s, 2H, CHO), 7.00 (s, 2H, Th-H),4.36 (t, $^3J_{Hη\text{-}Hϑ}$*= 5.4 Hz*, 2H, Hη), 4.08 (t, $^3J_{Hϑ\text{-}Hη}$ *= 5.5 Hz*, 2H, Hθ), 2.96-2.92 (m, 8H, Hα, Hα‘), 1.81-1.68 (m, 8H, Hβ, Hβ‘), 1.44-1.32 (m, 24H, Hγ-Hε, Hγ‘-Hε‘), 0.93-0.88 (m, 15H, Hζ, Hζ‘, Hι), 0.81-0.80 (m, 18H, Hκ); ^{13}C-NMR (101 MHz, $CDCl_3$, UDEFT): δ [ppm] = 181.5, 153.5, 145.9, 141.8, 136.1, 135.9, 135.6, 128.6, 127.6, 122.0, 118.6, 63.2, 50.7, 31.7, 31.5, 29.5, 29.2, 29.2, 29.1, 28.7, 22.8, 22.7, 17.7, 14.2, 11.9; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{57}H_{81}NO_3S_6Si$: m/z = 1047.4305; found: m/z = 1047.4302 (δm/m = 0.21ppm).

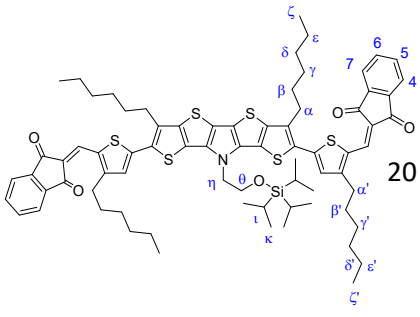
5,5'-[3,6-Dihexyl-9-(2-hydroxyethyl)-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]pyrrole-2,7-diyl]bis(3-hexylthiophene-2-carbaldehyde) ***26****.* Aldehyde **25** (100 mg, 95.4 µmol) was dissolved in THF (8 mL) and TBAF solution (1M in THF, 1.43 mL, 1.43 mmol) was added. The mixture was stirred at r.t. for 2.5 h. Afterwards, the solvent was removed under reduced pressure. The remaining solid was dissolved in DCM and precipitated from methanol. After filtration, alcohol **26** (85.1 mg, 95.4 µmol, 99.9%) was obtained as a dark red solid in quantitative yield. Alcohol **26** was precipitated and filtered from methanol. Mp 203.8-206.7 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 9.94 (s, 2H, CHO), 7.03 (s, 2H, Th-H), 4.46-4.45 (m, 2H, Hη), 4.14 (m, 2H, Hθ), 2.96-2.91 (m, 8H, Hα, Hα‘), 2.02 (s, 1H, OH), 1.79-1.70 (m, 8H, Hβ, Hβ‘), 1.47-1.35 (m, 24H, Hγ-Hε, Hγ‘-Hε‘) 0.91 (m, 12H, Hζ, Hζ‘); ^{13}C-NMR (101 MHz, $CDCl_3$, UDEFT): δ [ppm] = 181.5, 153.5, 145.6, 142.1, 136.3, 135.8, 135.7, 128.9, 127.8, 121.8, 118.8, 31.7, 31.5, 29.6, 29.2, 29.1, 28.7, 22.8, 22.7, 14.2, 14.2; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{48}H_{61}NO_3S_6$: m/z= 891.2970; found: m/z = 891.2967 (δm/m = 0.31ppm).



2,2'-{[[3,6-Dihexyl-9-(2-[(triisopropylsilyl)oxy)ethyl]-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]-thieno[2,3-d]pyrrole-2,7-diyl]bis(3-hexylthiophene-5,2-diyl)]bis(methaneylylidene)}dimalononitrile ***R17***. Dialdehyde **26** (40.0 mg, 38.1 µmol), malononitrile (101 mg, 1.53 mmol) and ammonium acetate (118 mg, 1.53 mmol) were dissolved in DCE (8 mL) and the mixture was stirred at 80 °C for 16 h until TLC revealed completed conversion. Afterwards, the solvent was removed under reduced pressure and the residue was dissolved in a small amount of DCM and precipitated in methanol. After filtration, the remaining solid was again dissolved in DCM and filtered over a patch of silica gel to obtain the pure product **R17** (43.7 mg, 38.1 µmol, 99.9%) as a dark solid which was precipitated and filtered from methanol. Mp 246.4-248.0 °C ; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.74 (s, 2H, vinyl-H), 7.06 (s, 2H, Th-H), 4.39-4.37 (t, $^{3}J_{Hη\text{-}Hϑ}$= *5.1 Hz*, 2H, Hη), 4.09-4.07 (m, 2H, Hθ), 2.95 (t, $^{3}J_{Hα\text{-}Hβ}$= *8.0 Hz*, 4H, Hα), 2.75 (t, $^{3}J_{Hα'\text{-}Hβ'}$= *7.8 Hz*, 4H, Hα'),1.80-1.63 (m, 8H, Hβ', Hβ) 1.52-1.34 (24H, Hγ-Hε, Hγ'-Hε'), 0.97-0.75 (m, 33H, Hζ, Hζ', Hι, Hκ); ^{13}C-NMR (101 MHz, $CDCl_3$, UDEFT): δ [ppm] = 156.5, 147.5, 146.9, 142.8, 137.3, 136.4, 129.0, 128.5, 126.3, 122.9, 119.6, 115.4, 114.3, 77.4, 73.1, 63.2, 50.9, 31.8, 31.7, 31.3, 29.7, 29.6, 29.3, 29.3, 29.1, 22.7, 17.7, 14.2, 11.9 ; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{63}H_{81}N_5OS_6Si$: m/z = 1143.4529; found: m/z = 1143.4529 (δm/m = 0.02 ppm).

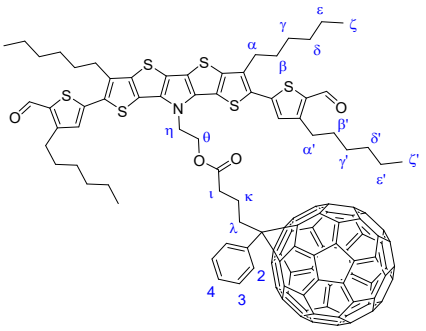


2,2'-{[[3,6-Dihexyl-9-[2-[(triisopropylsilyl)oxy]ethyl]-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]-thieno[2,3-d]pyrrole-2,7-diyl]bis(3-hexylthiophene-5,2-diyl)]bis(methaneylylidene)}bis[1H-indene-1,3 (2H)-dione] ***R18***. Dialdehyde **26** (39.6 mg, 37.8 µmol) and 1,3-indandione (22.1 mg, 0.15 mmol) were dissolved in DCE (8 mL) and one drop of piperidine was added. The mixture was stirred at r.t. for 16 h until TLC revealed completed conversion. Afterwards, the solvent was removed under reduced pressure and the residue was dissolved in a small amount of DCM and precipitated in methanol. After filtration, the remaining solid was again dissolved in DCM and filtered over a patch of silica gel to obtain the pure product **R18** (49.3 mg, 37.8 µmol, 99.9%) as a dark solid in quantitative yield. Mp 294.4-296.0 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.91-7.89 (m, 4H, H7, H4), 7.83-7.81 (m, 2H, vinyl-H), 7.70-7.61 (m, 4H, H5, H6), 7.01 (s, 2H, Th-H), 4.37 (t, $^{3}J_{Hη\text{-}Hϑ}$= *5.2 Hz*, 2H, Hη), 4.09-4.06 (m, 2H, Hθ), 3.04 (t, $^{3}J_{Hα\text{-}Hβ}$= *7.8 Hz*, 4H, Hα), 2.89 (t, $^{3}J_{Hα'\text{-}Hβ'}$= *7.8 Hz*, 4H, Hα'), 1.89-1.81 (m, 4H, Hβ), 1.75-1.68 (m, 4H, Hβ'), 1.62-1.55 (m, 4H, Hγ), 1.47-1.35 (m, 20H, Hδ-Hε, Hγ'-Hε'), 0.95-0.84 (m, 15H, Hζ, Hζ', Hι), 0.78-0.76 (m, 18H, Hκ). ^{13}C-NMR (101 MHz, $CDCl_3$, UDEFT): δ [ppm] = 190.7, 189.5, 157.9, 148.4, 142.7, 142.1, 140.4, 136.4, 136.3, 134.6, 134.3, 132.2, 131.1, 129.9, 126.6, 122.7, 122.5, 121.5, 119.2,

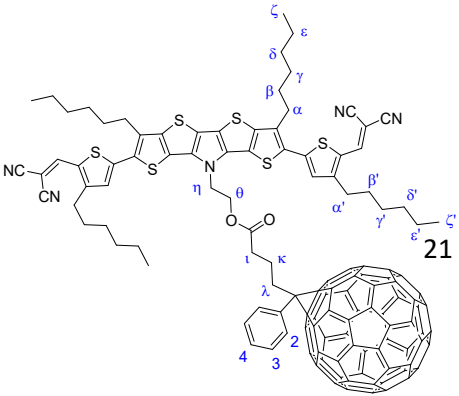


63.3, 50.7, 31.8, 31.5, 29.8, 29.7, 29.6, 29.3, 29.0, 22.9, 22.8, 17.7, 14.3, 14.3, 11.9; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{75}H_{89}NO_5S_6Si$: m/z = 1303.4829; found: m/z = 1303.4830 (δm/m = 0.05 ppm).

*6,6-Phenyl-C_{61}-butyric acid {2-[2,7-bis(5-formyl-4-hexylthiophen-2-yl)-3,6-dihexyl-9H-thieno[2',3':4,5]-thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]pyrrol-9-yl]ethyl} ester **27**.* PCBA (103 mg, 114 µmol) and alcohol **26** (85.0 mg, 95.3 µmol) were dissolved in a solvent mixture of dry chlorobenzene and carbon disulfide (85 mL, 2:1) and DMAP (16.3 mg, 133 µmol) and EDC x HCl (22.6 mg, 118 µmol) were added. The mixture was treated with some drops of TEA and stirred at 40 °C for 4 days. The solvent was removed under reduced pressure and crude purification was done via column chromatography over flash silica gel (DCM/Et_2O 95:5) followed by purification via SEC (DCM) to obtain dyad **27** (155 mg, 87.6 µmol, 91.9%) as a brown solid which was precipitated from methanol. Mp > 360 °C (DSC); ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 10.00 (s, 2H, CHO), 7.72-7.69 (m, 2H, H2), 7.41-7.37 (m, 3H, H3, H4), 7.01 (s, 2H, Th-H), 4.48 (s, 4H, Hθ, Hη), 2.95-2.91 (m, 8H, Hα, Hα'), 2.64-2.60 (m, 2H, Hλ), 2.39 (t, $^3J_{Hι-Hκ}$ = *6.9 Hz*, 2H, Hι), 1.94-1.87 (m, 2H, Hκ), 1.80-1.67 (m, 8H, Hβ, Hβ'), 1.47-1.29 (m, 24H, Hγ-Hε, Hγ'-Hε'), 0.92 – 0.88 (m, 12H, Hζ, Hζ'); ^{13}C-NMR (101 MHz, $CDCl_3$, UDEFT): δ [ppm] = 181.5, 172.7, 153.5, 148.8, 147.7, 145.7, 145.5, 145.2, 145.1, 145.1, 144.8, 144.7, 144.7, 144.6, 144.3, 144.0, 143.8, 143.7, 143.0, 143.0, 142.9, 142.3, 142.2, 142.1, 142.1, 142.0, 140.9, 140.7, 137.8, 137.6, 136.6, 136.5, 135.8, 135.7, 132.0, 128.9, 128.5, 128.3, 127.9, 121.5, 119.2, 63.6, 47.3, 33.6, 32.9, 31.8, 31.7, 31.7, 29.7, 29.3, 29.1, 28.7, 22.8, 22.7, 22.0, 14.3, 14.3; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{119}H_{71}NO_4S_6$: m/z = 1770.3734; found: m/z = 1770.3726 (δm/m = 0.43 ppm).

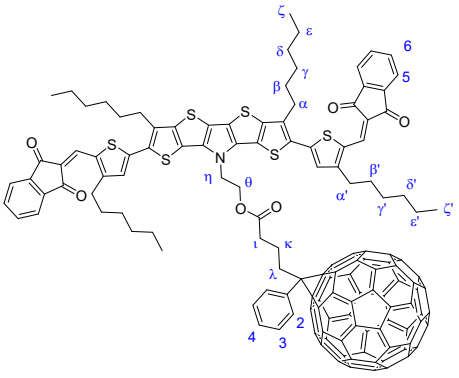


*6,6-Phenyl-C_{61}-butyric acid {2-[2,7-bis[5-(2,2-dicyanovinyl)-4-hexylthien-2-yl]-3,6-dihexyl-9H-thieno[2', 3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno [2,3-d]pyrrol-9-yl}ethyl ester **D17**.* Dialdehyde **27** (70.0 mg, 39.5 µmol), malononitrile (157 mg, 2.37 mmol) and ammonium acetate (183 mg, 2.37 mmol) were dissolved in DCE (13.2 mL) and the mixture was stirred at 80 °C for 15 h until TLC revealed completed conversion. Afterwards, the solvent was removed under reduced pressure and the residue was dissolved in a small amount of DCM and precipitated in methanol. After filtration, the remaining solid was purified via column chromatography (DCM:Et_2O 5%) to obtain the pure product **D17** (67.1 mg, 39.5 µmol, 90.9%) as a dark solid which was precipitated and filtered from methanol. Mp 299.45 °C (DSC

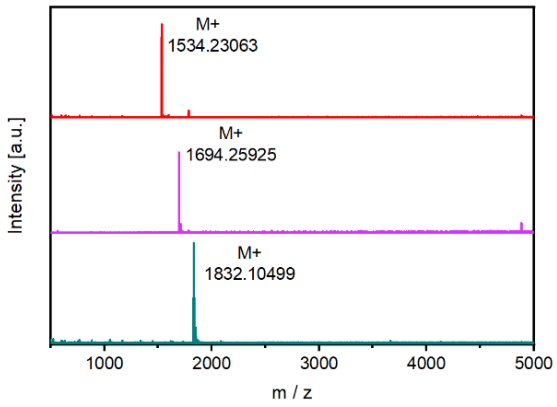


Peak onset); ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.76 (s, 2H, vinyl-H), 7.71-7.69 (m, 2H, H2), 7.41 - 7.38 (m, 3H, H4, H3), 7.07 (s, 2H, Th-H), 4.51-4.48 (m, 4H, Hθ, Hη), 2.94 (t, $^{3}J_{Hα\text{-}Hβ}$ = *8.2 Hz*, 4H, Hα), 2.76-2.72 (m, 4H, Hα'), 2.64-2.60 (m, 2H, Hλ), 2.39 (t, $^{3}J_{Hι\text{-}Hκ}$ = *6.9 Hz*, 2H, Hι), 1.92-1.85 (m, 2H, Hκ), 1.80-1.72 (m, 4H, Hβ), 1.69-1.62 (m, 4H, Hβ'), 1.52-1.33 (m, 24H, Hγ-Hε, Hγ'-Hε'), 0.94 – 0.89 (m, 12H, Hζ, Hζ'); ^{13}C-NMR (101 MHz, $CDCl_3$, UDEFT): δ [ppm] = 172.6, 156.6, 148.7, 147.7, 147.0, 147.0, 145.7, 145.3, 145.2, 145.1, 145.0, 144.9, 144.7, 144.7, 144.6, 144.3, 144.1, 143.8, 143.7, 143.1, 143.0, 143.0, 142.9, 142.2, 142.2, 142.1, 142.0, 140.9, 140.8, 137.8, 137.6, 137.4, 136.6, 136.1, 132.0, 129.3, 128.7, 128.5, 128.4, 126.6, 122.3, 120.1, 115.3, 114.2, 79.7, 73.7, 63.4, 51.4, 47.4, 33.5, 32.9, 31.7, 31.5, 29.8, 29.7, 29.4, 29.4, 29.2, 22.8, 21.9, 14.3, 14.3; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{125}H_{71}N_5O_2S_6$: m/z = 1866.3958; found: m/z = 1866.3944 (δm/m = 0.76 ppm).

*6,6-Phenyl-C_{61}-butyric acid{2-[2,7-bis[5-[(1,3-dioxo-1,3-dihydro-2H-inden-2-ylidene)methyl]-4-hexylthien-2-yl]-3,6-dihexyl-9H-thieno[2',3':4,5]thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]pyrrol-9-yl]ethyl} ester **D18**.* Dialdehyde **27** (70.0 mg, 39.5 µmol) and 1,3-indandione (23.1 mg, 158 µmol) were dissolved in DCE (17.5 mL) and one drop of piperidine was added. The mixture was stirred at r.t. for 21 h. Afterwards, the solvent was removed under reduced pressure and the residue was dissolved in a small amount of DCM and precipitated in methanol. After filtration, the remaining solid was again dissolved in DCM and purified via column chromatography (flash silica gel, DCM:Et_2O 97:3) to obtain **D18** (52.1 mg, 25.6 µmol, 65.0%) as a dark solid. Mp.: 279.6 °C (DSC peak onset); ^{1}H-NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.89-7.79 (m, 6H, vinyl-H, H5), 7.69-7.59 (m, 6H, H6, H2), 7.35-7.31 (m, 3H, H3, H4), 6.97 (s, 2H, Th-H), 4.47 (s, 4H, Hθ, Hη), 2.99-2.95 (m, 4H, Hα), 2.86 (t, $^{3}J_{Hα'\text{-}Hβ'}$ = *7.8 Hz*, 4H, Hα'), 2.62-2.58 (m, 2H, Hλ), 2.39 (t, $^{3}J_{Hι\text{-}Hκ}$ = *6.9 Hz*, 2H, Hι), 1.91-1.78 (m, 6H, Hκ, Hβ), 1.73-1.57 (m, 8H, Hβ', Hγ), 1.47-1.35 (m, 20H, Hδ-Hε, Hγ'-Hε'), 0.96-0.91 (m, 12H, Hζ, Hζ'); ^{13}C-NMR (101 MHz, $CDCl_3$, UDEFT): δ [ppm] = 190.5, 189.5, 172.7, 157.9, 148.8, 147.9, 147.7, 145.6, 145.2, 145.2, 145.1, 145.0, 144.8, 144.7, 144.5, 144.2, 144.0, 143.8, 143.7, 143.0, 143.0, 142.9, 142.2, 142.1, 142.0, 140.9, 140.7, 140.3, 137.9, 137.5, 136.6, 136.3, 136.0, 134.7, 134.3, 132.0, 132.0, 131.2, 130.0, 128.4, 128.2, 126.6, 122.7, 122.5, 121.9, 121.8, 119.6, 79.8, 63.6, 51.5, 47.3, 33.6, 33.0, 31.9, 31.6, 29.9, 29.8, 29.7, 29.5, 29.0, 22.9, 22.8, 21.9, 14.4, 14.3; HR-MS (FTICR-MALDI): $[M]^+$ calculated for $C_{137}H_{79}NO_6S_6$: m/z = 2026.4259; found: m/z = 2026.4290 (δm/m = 1.57 ppm).



3. High resolution mass spectra of dyads D11-D18 and reference compounds R11-R18



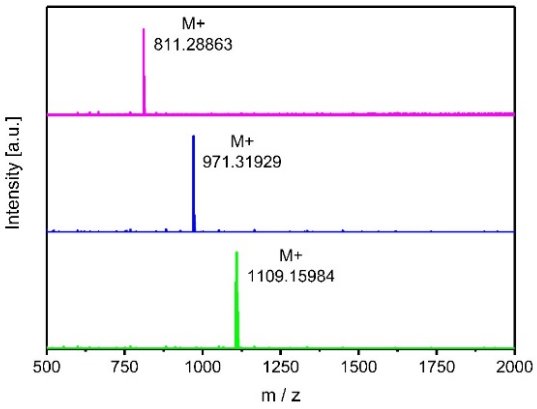


Figure S1: HR-MALDI FTICR mass spectra of SN5'-based **D11** (red), **D12** (purple), and **D13** (dark green) (left) and TIPS-protected reference compounds **R11** (pink), **R12** (blue), and **R13** (green) (right) with DCTB as matrix.

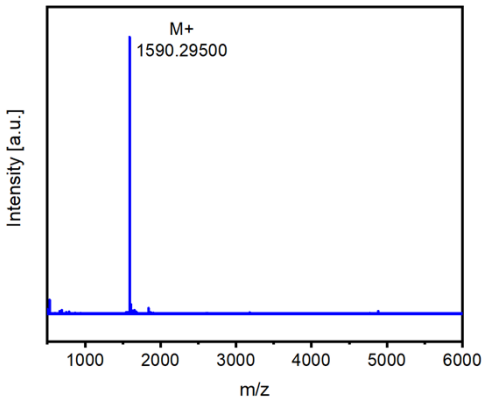


Figure S2: HR-MALDI FTICR mass spectra of SN5'-based **D14** (blue) with DCTB as matrix.

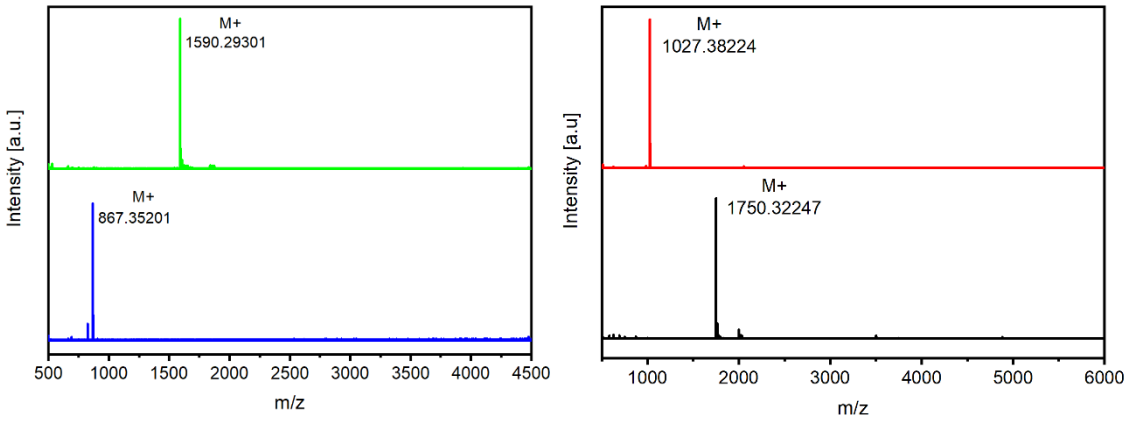


Figure S3: HR-MALDI FTICR mass spectra of SN5'-based **D15** (green) and **R15** (blue) (left) and **D16** (black), **R16** (red) (right)with DCTB as matrix.

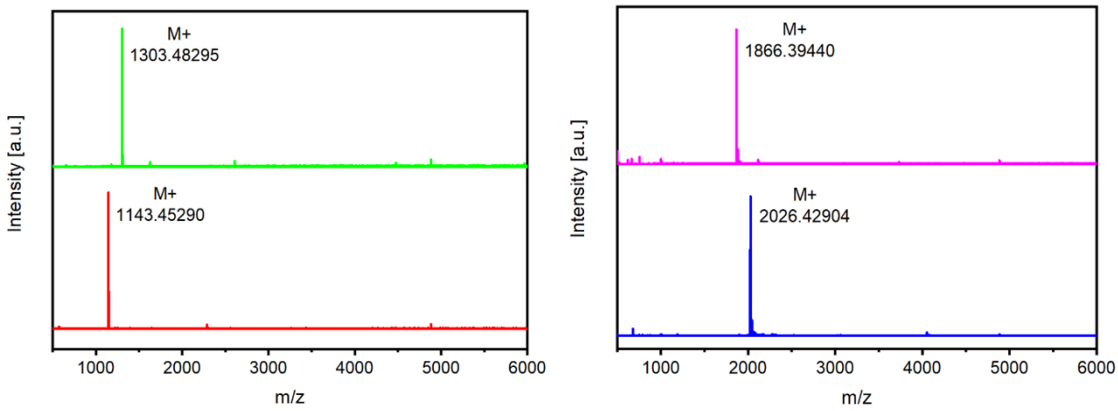


Figure S4: High resolution MALDI FTICR mass spectra of the reference compounds **R18** (green), **R17** (red), and the dyads **D17** (pink) and **D18** (blue) with DCTB as matrix.

4. Optical Properties of dyads D11-D18 and reference compounds R11-R18

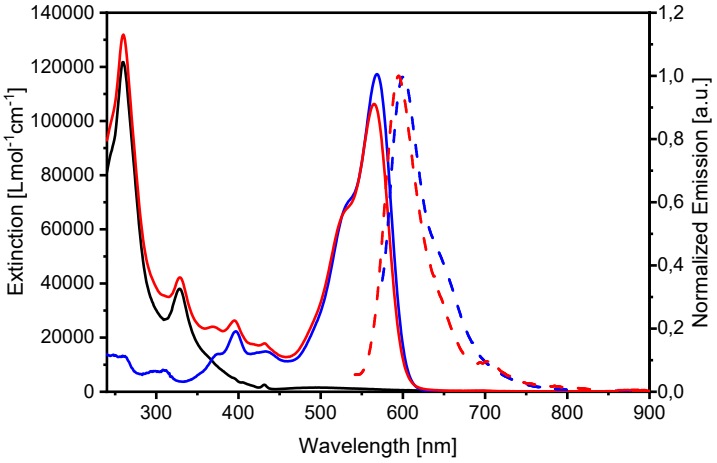


Figure S5: Solution absorption spectra (continuous lines) and normalized emission (dashed lines) of TIPS-protected SN5'-derivative **R11** (blue), $PC_{61}BM$ (black), and **D11** (red) recorded in DCM solution. Excitation wavelength was at 570 nm (**R11**) and 520 nm (**D11**).

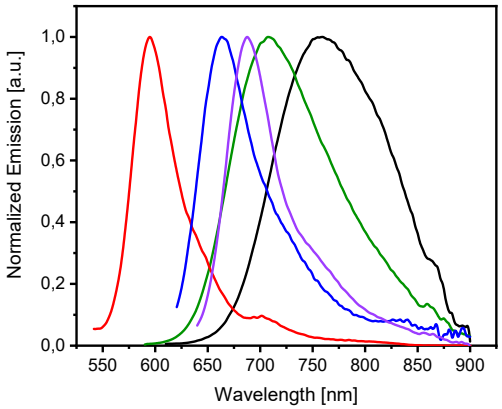


Figure S6: Normalized emission spectra of **D11** (red), **D12** (blue), **D13** (purple), **D17** (green), and **D18** (black) recorded in DCM solution. Excitation wavelength 520 nm (**D11**), 640 nm (**D12**), 680 nm (**D13**), 570 nm (**D17**), 590 nm (**D18**).

5. Electrochemical Properties

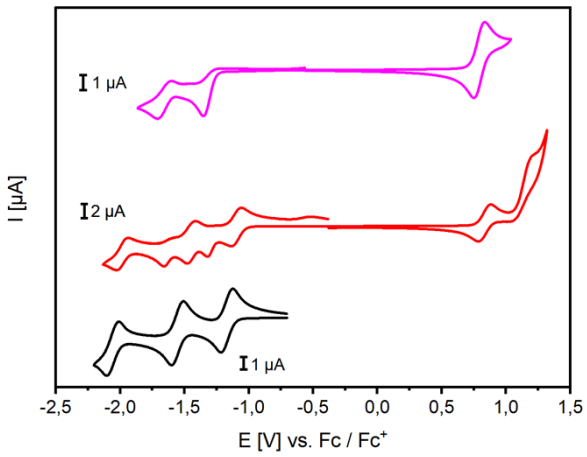


Figure S7: Cyclic voltammograms of the **D11** (red), **R11** (pink), and **$PC_{61}BM$** (black) found in DCM solution, using $TBAPF_6$ as conducting salt and Fc/Fc^+ as internal standard, scan speed 0.1 Vs^{-1}**.**

6. Optimization of single-material organic solar cells (SMOSC)

*Dyad **D11***. Different solvents were tested for the processing of the active layer of SMOSCs with **D11**:CF (rt), CB (80°C), oDCB (80 °C), toluene (80°C), TCE (80°C) on glass substrates at the same temperature as the solution. Solvent vapor annealing (SVA) was performed with CS_2, THF, and CF for 10s, 20s, 30s, respectively. The highest achieved efficiency of 0.07% was obtained by processing from CB (80°C) in a concentration of 15 mg mL^{-1} at a rotation speed of 2000 rpm after 30 s solvent vapor annealing (SVA) with THF (table S1).

Table S1: SMOSCs with dyad **D11** in the active layer and different SVA solvents.

	SVA	**V_{OC}** [V]	**J_{sc}** [mA/cm²]	**FF**	**PCE** [%]
A	-	0.47±0.03 (0.51)	0.28±0.01 (0.29)	0.29±0.00 (0.30)	0.04±0.00 (0.04)
B	10 s CS_2	0.66±0.03 (0.69)	0.31±0.03 (0.34)	0.27±0.00 (0.30)	0.05±0.01 (0.06)
C	20 s CS_2	0.63±0.08 (0.70)	0.29±0.02 (0.33)	0.27±0.01 (0.30)	0.05±0.01 (0.06)
D	30 s CS_2	0.67±0.01 (0.68)	0.31±0.00 (0.32)	0.26±0.00 (0.27)	0.05±0.00 (0.06)
E	20 s THF	0.66±0.01 (0.67)	0.30±0.00 (0.30)	0.27±0.00 (0.27)	0.05±0.00 (0.05)
F	30 s THF	0.68±0.03 (0.70)	0.32±0.02 (0.36)	0.26±0.00 (0.27)	0.06±0.00 (**0.07**)

Average value of four cells ± standard deviation (maximum); cell architecture: glass/ ITO/ PEDOT:PSS/ **D11** in CB, 15 mg mL^{-1}, 80 °C, 2000 rpm/ LiF/ Al.

*Dyad **D12.*** Different solvents were tested for the processing of the active layer of SMOSCs with **D12**: CF (50 °C), CB (50 °C and rt), oDCB (50 °C), THF (50°C) on glass substrates at rt. SVA was performed with CS_2, THF, DCM, and CF for 10s, 20s, 30s, respectively. The highest achieved efficiency of 0.26% was obtained by processing from CB (rt) in a concentration of 15 mg mL^{-1} at a rotation speed of 3000 rpm after 10s CS_2 (Table S2).

Table S2: SMOSCs with dyad **D12** in the active layer and different SVA solvents.

	v [rpm]	**SVA**	**V_{OC}** [V]	**J_{sc}** [mA/cm²]	**FF**	**PCE** [%]
A	3000	-	0.72±0.09 (0.79)	1.26 ±0.10 (1.35)	0.25±0.01 (0.27)	0.23±0.03 (0.26)
B	3000	10 s CS_2	0.79±0.01 (0.80)	1.32 ±0.03 (1.35)	0.24±0.00 (0.24)	0.25±0.01 (**0.26**)

Average value of four cells ± standard deviation (maximum); cell architecture: glass/ ITO/ PEDOT:PSS/ **D12** in CB, 15 mg mL^{-1}, rt, 3000 rpm/ LiF/ Al.

*Dyad **D13*** showed poor solubility in most organic solvents. Nevertheless, for the processing of the active layer different solvents were tested: CF (50 °C), THF (50 °C), CB (50 °C and 80 °C), anisole (50 °C), toluene (50 °C), DCE (50 °C), oDCB (80°C), TCE (80 °C), DMF (80 °C), and tetrachloroethylene (80°C). The highest achieved efficiency of 0.04% was obtained by processing from CF (50 °C) in a concentration of 15 mg mL^{-1} at a rotation speed of 3000 rpm (Table S3).

Table S3: SMOSCs with dyad **D13** in the active layer.

	v [rpm]	**V_{OC}** [V]	**J_{sc}** [mA/cm²]	**FF**	**PCE** [%]
A	2000	0.60±0.05 (0.66)	0.15±0.00 (0.16)	0.29±0.01 (0.30)	0.03±0.00 (0.03)
B	3000	0.68±0.05 (0.75)	0.19±0.00 (0.20)	0.28±0.01 (0.29)	0.04±0.00 (**0.04**)

Average value of four cells ± standard deviation (maximum); cell architecture: glass/ ITO/ PEDOT:PSS/ **D13** in CF, 15 mg mL^{-1}, 50 °C/ LiF/ Al.

*Dyad **D14.*** Different solvents were tested for the processing of the active layer of SMOSCs with **D14**: CF (stirred at 50 °C, processed at r.t.) on glass substrates at r.t. SVA was performed with CS_2, THF, and CF for 30s, respectively. The highest achieved efficiency of 0.03% was obtained by processing from CF in a concentration of 15 mg mL^{-1} at a rotation speed of 2000 rpm followed by SVA with CS_2 for 30 s (Table S4).

Table S4: SMOSCs with dyad **D14** in the active layer and different SVA solvents.

	SVA	V_{OC} [V]	J_{sc} [mA/cm²]	FF	PCE [%]
A	-	0.31±0.18 (0.50)	0.19±0.00 (0.19)	0.23±0.04 (0.28)	0.01±0.01 (0.03)
B	30s CF	0.46±0.11 (0.62)	0.15±0.02 (0.17)	0.28±0.03 (0.32)	0.02±0.00 (0.02)
C	30s CS_2	0.67±0.12 (0.78)	0.13±0.01 (0.14)	0.25±0.01 (0.26)	0.02±0.00 (**0.03**)
D	30s THF	0.67±0.16 (0.82)	0.13±0.00 (0.14)	0.24±0.01 (0.26)	0.02±0.00 (0.02)

Average value of four cells ± standard deviation (maximum); cell architecture: glass/ ITO/ PEDOT:PSS/ **D14** in CF, 15 mg mL^{-1}, rt, 2000 rpm/ LiF/ Al.

*Dyad **D15***. The highest achieved efficiency of 0.04% (**A**) was obtained by processing from CF in a concentration of 15 mg mL^{-1} at a rotation speed of 1000 rpm (Table S5).

Table S5: SMOSCs with dyad **D15** in the active layer.

	SVA	v [rpm]	V_{OC} [V]	J_{sc} [mA/cm²]	FF	PCE [%]
A	-	1000 rpm	0.39±0.14 (0.60)	0.26±0.01 (0.28)	0.27±0.01 (0.28)	0.03±0.01 (**0.04**)
B	-	2000 rpm	0.60±0.04 (0.63)	0.15±0.09 (0.22)	0.19±0.03 (0.24)	0.02±0.01 (0.02)
C	-	3000 rpm	0.43±0.06 (0.48)	0.11±0.02 (0.13)	0.14±0.02 (0.17)	0.01±0.00 (0.01)

Average value of four cells ± standard deviation (maximum); cell architecture: glass/ ITO/ PEDOT:PSS/ **D15** in CF, 15 mg mL^{-1}, rt/ LiF/ Al.

*Dyad **D16**.* A CF solution of the dyad was spin-coated with following SVA with CS_2 for different times. The summarized results are shown in Table S6. Experiment **A** delivered an average efficiency of 1.33% without SVA. The fill factor and current density are low, but the open circuit voltage with 1.06 V is close to the theoretical 1.20 V. SVA with CS_2 for 20 s (**C**) led to significant increase in current density and PCE (2.83%).

Table S6: SMOSCs with **D16** in the active layer and different SVA times.

	SVA	v [rpm]	V_{OC} [V]	J_{sc} [mA/cm²]	FF	PCE [%]
A	-	2000 rpm	1.06±0.00 (1.06)	4.74±0.23 (4.93)	0.27±0.00 (0.27)	1.33±0.05 (1.38)
B	10 s CS_2	2000 rpm	1.05±0.00 (1.05)	5.88±0.05 (5.94)	0.28±0.02 (0.29)	1.73±0.11 (1.81)
C	20 s CS_2	2000 rpm	1.04±0.00 (1.04)	7.44±0.49 (7.95)	0.34±0.01 (0.35)	**2.63±0.21 (2.83)**
D	30 s CS_2	2000 rpm	1.01±0.00 (1.01)	7.48±0.18 (7.66)	0.32±0.00 (0.32)	2.41±0.06 (2.49)
E	40 s CS_2	2000 rpm	1.00±0.01 (1.02)	6.39±0.23 (6.64)	0.29±0.01 (0.30)	1.88±0.11 (1.96)

Average value of four cells ± standard deviation (maximum); cell architecture: glass/ ITO/ PEDOT:PSS/ **D16** in CF, 15 mg mL^{-1}, rt/ LiF/ Al.

*Dyad **D17*** was dissolved in different solvents: CB (rt), oDCB (rt), THF (rt), and DCM (rt). The active layer processed from CB and oDCB was very thin due to the high boiling points of the solvents. THF led to smooth and homogenous films, however, no photovoltaic effect could be measured. The films spin-coated from DCM are not as homogeneous as the THF films and also led to a PCE of 0%. The CF films appeared smooth and SVA post-treatment with three different solvents was performed (CF, CS_2, THF). The results are shown in Table S7. Low or no current densities led to efficiencies of 0%. The fill factor around 13% was as well very low and the open circuit voltage couldn't exceed 0.50 V.

Table S7: SMOSCs with dyad **D17** in the active layer and different SVA solvents.

	SVA	**V_{OC}** [V]	**J_{sc}** [mA/cm²]	**FF**	**PCE** [%]
A	-	0.48±0.07 (0.58)	0.02±0.01 (0.03)	0.13±0.03 (0.18)	0.00
B	20 s CF	0.44±0.03 (0.48)	0.01±0.00 (0.01)	0.13±0.02 (0.17)	0.00
C	40 s CF	0.46±0.03 (0.50)	0.01±0.00 (0.02)	0.13±0.01 (0.14)	0.00
D	20 s CS_2	0.41±0.04 (0.47)	0.00±0.00 (0.00)	0.17±0.02 (0.20)	0.00
E	40 s CS_2	0.43±0.07 (0.52)	0.00±0.00 (0.01)	0.16±0.01 (0.18)	0.00
F	20 s THF	0.31±0.12 (0.44)	0.00±0.00 (0.00)	0.17±0.03 (0.22)	0.00
G	40 s THF	0.41±0.03 (0.46)	0.01±0.00 (0.01)	0.13±0.01 (0.14)	0.00

Average value of four cells ± standard deviation (maximum); cell architecture: glass/ ITO/ PEDOT:PSS/ **D17** in CF, 15 mg mL^{-1}, rt, 2000 rpm/ LiF/ Al.

*Dyad **D18*** with elongated π-system and IND-acceptor was tested in SMOSCs. CF, CB, THF, and oDCB were used as processing solvents at different rotation speeds 1000-3000 rpm. The results of this optimization are summarized in Table S8, THF is not listed due to inhomogeneous films and low solubility. The highest efficiencies were obtained with CF at a rotation speed of 3000 rpm with a maximum efficiency of 0.37% (**C**). This condition was kept for further optimization. Table S9 shows the optimization of SVA solvent and time. After 20 s SVA treatment with CS_2, a maximum efficiency of 0.86% (**E**) was achieved. This is over twice as high as the cells before post-treatment. The average fill factor of 34% (**E**) is low compared to the BHJSCs of the reference compound.

Table S8: SMOSCs with dyad **D18** in the active layer with different processing conditions.

	Solvent	v [rpm]	V_{OC} [V]	J_{sc} [mA/cm²]	FF	PCE [%]
A	CF (rt)	1000	0.86±0.00 (0.86)	1.22±0.03 (1.26)	0.27±0.01 (0.27)	0.28±0.01 (0.29)
B	CF (rt)	2000	0.87±0.01 (0.87)	1.67±0.02 (1.68)	0.25±0.00 (0.25)	0.36±0.00 (0.36)
C	CF (rt)	3000	0.87±0.01 (0.88)	1.76±0.02 (1.78)	0.24±0.00 (0.24)	0.37±0.01 (**0.37**)
D	CB (50 °C)	2000	0.80±0.01 (0.81)	0.49±0.08 (0.57)	0.20±0.01 (0.21)	0.08±0.01 (0.10)
E	CB (50 °C)	3000	0.77±0.02 (0.79)	0.24±0.17 (0.46)	0.22±0.02 (0.24)	0.04±0.03 (0.08)
F	oDCB (50 °C)	2000	0.54±0.02 (0.57)	0.61±0.02 (0.63)	0.38±0.01 (0.39)	0.12±0.01 (0.14)
G	oDCB (50 °C)	3000	0.11±0.01 (0.12)	0.32±0.01 (0.33)	0.28±0.01 (0.28)	0.01±0.00 (0.01)

Average value of four cells ± standard deviation (maximum); cell architecture: glass/ ITO/ PEDOT:PSS/ **D18** 15 mg mL^{-1}, r.t. / LiF/ Al.

Table S9: SMOSCs with dyad **D18** in the active layer with different SVA conditions.

	SVA	V_{OC} [V]	J_{sc} [mA/cm²]	FF	PCE [%]
A	20 s CF	0.78±0.04 (0.81)	1.64±0.04 (1.68)	0.25±0.00 (0.25)	0.31±0.01 (0.33)
B	40 s CF	0.80±0.02 (0.82)	1.54±0.02 (1.57)	0.24±0.00 (0.24)	0.30±0.00 (0.30)
C	60 s CF	0.79±0.01 (0.80)	1.46±0.01 (1.47)	0.24±0.00 (0.24)	0.28±0.01 (0.28)
D	10 s CS_2	0.76±0.13 (0.84)	1.82±0.12 (0.91)	0.25±0.00 (0.25)	0.35±0.07 (0.40)
E	20s CS_2	0.68±0.01 (0.69)	3.11±0.10 (3.66)	0.34±0.01 (0.35)	0.81±0.04 (**0.86**)
F	40 s CS_2	0.64±0.01 (0.65)	3.11±0.14 (3.34)	0.33±0.01 (0.34)	0.66±0.03 (0.72)
G	60 s CS_2	0.60±0.02 (0.63)	2.54±0.21 (2.83)	0.31±0.01 (0.33)	0.48±0.02 (0.51)
H	20 s THF	0.83±0.01 (0.84)	0.79±0.46 (1.10)	0.23±0.01 (0.25)	0.15±0.09 (0.20)
I	40 s THF	0.81±0.02 (0.82)	0.90±0.06 (0.97)	0.22±0.00 (0.23)	0.16±0.01 (0.18)
J	60 s THF	0.72±0.15 (0.82)	0.85±0.08 (0.93)	0.24±0.02 (0.28)	0.14±0.03 (0.17)

Average value of four cells ± standard deviation (maximum); cell architecture: glass/ ITO/ PEDOT:PSS/ **D18** 15 mg mL^{-1}, rt / LiF/ Al.

7. Thermal properties

Differential scanning calorimetry (DSC)

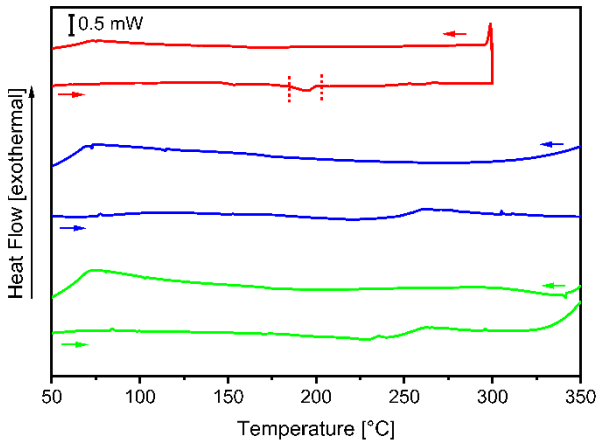


Figure S8: DSC traces of **D11** (red, above), **D12** (blue, middle), **D13** (green, below) under Argon flow with a heating rate of 10 °C/min.

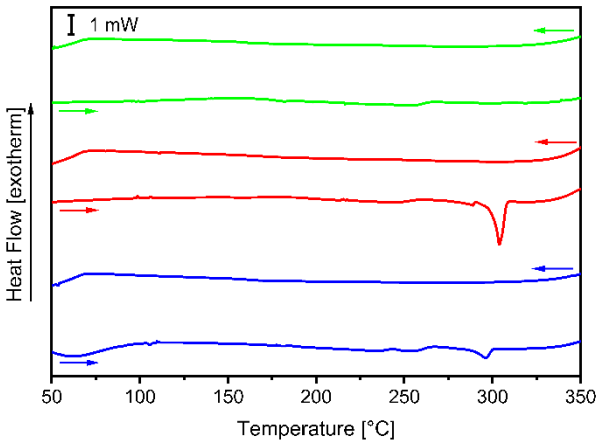


Figure S9: DSC traces of **D14** (green, above), **D15** (red, middle), and **D16** (blue, below) under Argon flow with a heating rate of 10 °C/min.

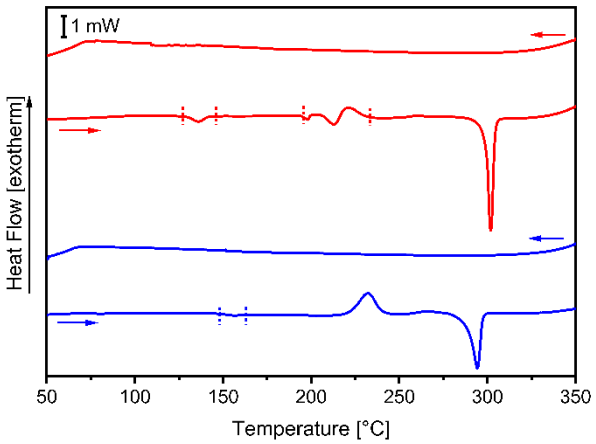


Figure S10: DSC traces of **D17** (red, above) and **D18** (blue, below) under Argon flow with a heating rate of 10 °C/min.

Thermal gravimetric analysis (TGA)

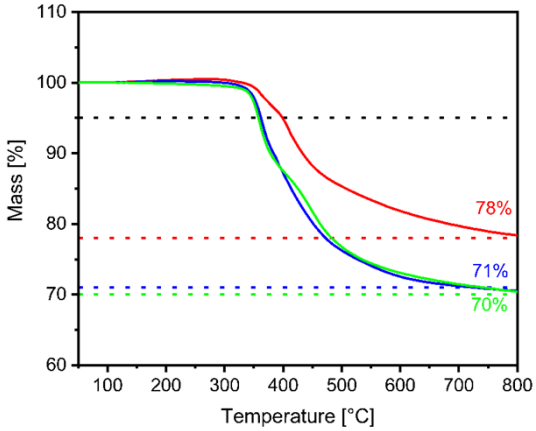


Figure S11: TGA traces of **D11** (red), **D12** (blue), and **D13** (green) (10 °C min^{-1} under Nitrogen flow).

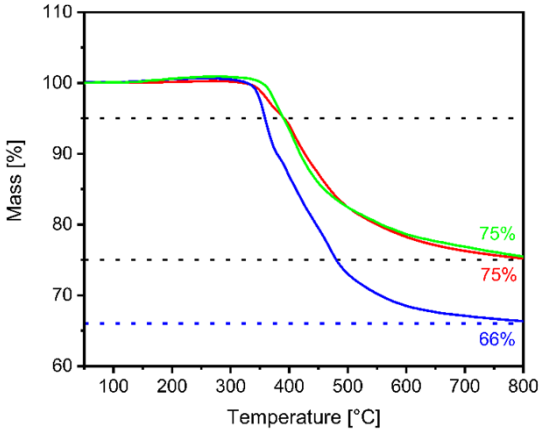


Figure S12: TGA traces of **D14** (green), **D15** (red), and **D16** (blue) (10 °C min^{-1} under Nitrogen flow).

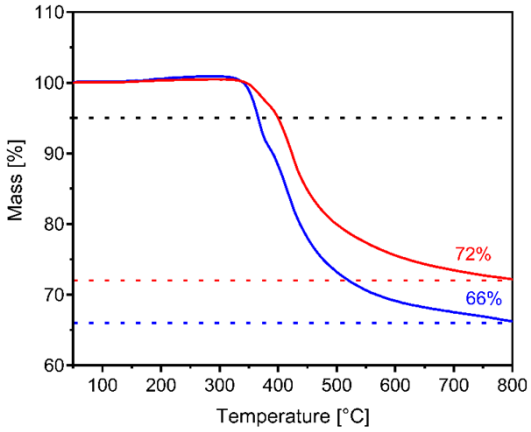


Figure S13: TGA traces of **D17** (red) and **D18** (blue) (10 °C min^{-1} under Nitrogen flow).

8. References

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