

## Electronic Supporting Info (ESI)

### Covalently Linked Donor-Acceptor Dyad for Efficient Single Material Organic Solar Cells

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## 1. Materials and methods

Solvents DCM (VWR), THF (Roth), DMF (VWR), and toluene (Roth) were dried and purified by a MB SPS-800 (MBraun). Pyridine, chlorobenzene, carbon disulfide, sodium *tert*-butoxide, malononitrile, 1,2-dichloroethane, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimid hydrochloride, and triethylamine were purchased from Merck. Tetrabutylammonium fluoride, tris(dibenzylideneacetone)dipalladium (0), trimethyltin chloride, pentafluorophenole, ethanolamine, butanolamine, and hexanolamine were obtained by Sigma-Aldrich. Chloroform, sodium chloride, and ammonium acetate were purchased from VWR. *n*-Butyl lithium was purchased from Acros Organics. (2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl) was purchased from Oxchem. Magnesium sulphate was purchased from Grüsing GmbH. *N,N*-dimethyl-4-aminopyridine was purchased from Alpha Aesar. Preparative column chromatography was performed on class columns filled with silica 60 and silica 60 M by Macherey+Nagel. 1,1'-Bis(diphenylphosphino)ferrocene was purchased by Fluorochem. [6,6]-Phenyl-C61-butyric acid was purchased from SolenneBV. 3,3'-Dibromo-2,2'-bithiophene **1**,<sup>1</sup> 5'-bromo-3,4'-dihexyl-2,2'-bithiophene-5-aldehyde **5**,<sup>2</sup> 4-[(triisopropylsilyloxy]butan-1-amine **2**,<sup>3</sup> tetrakis(triphenylphosphine)palladium(0),<sup>4</sup> reference compound 2,2'-[(4-(2-hexyldecyl)dithieno-[3,2-*b*:2',3'-*d*]pyrrole-2,6-diyl)bis((3,4'-dihexyl-2,2'-bithien-5,5'-diyl)bis(methane-1-yl-1-ylidene))]dimalononitrile<sup>2</sup> were synthesized according to literature. [6,6]-Phenyl-C61-butyric acid methyl ester (PC<sub>61</sub>BM, purity 99 %) was purchased from Solenne BV.

NMR spectra were recorded on a Bruker DRX 400 (<sup>1</sup>H-NMR 400 MHz, <sup>13</sup>C-NMR 101 MHz) and on a Bruker AMX 500 (<sup>1</sup>H-NMR 500 MHz, <sup>13</sup>C-NMR 125 MHz). Partially, uniform driven equilibrium Fourier transform (UDEFT) <sup>13</sup>C-NMR was performed, providing special pulse sequences,<sup>5</sup> in order to achieve higher resolution for quaternary carbon atoms. Residual solvent signals were used as internal standard (CDCl<sub>3</sub>: <sup>1</sup>H-NMR 7.26 ppm, <sup>13</sup>C-NMR 77.37 ppm; C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>: <sup>1</sup>H-NMR 6.00 ppm, <sup>13</sup>C-NMR 73.78 ppm). The NMR splitting patterns are abbreviated as: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Gas chromatography was performed on a Shimadzu GC-2010 Plus, GCMS on a Shimadzu GCMS-QP2010 SE. Melting points were determined with a Büchi M-565 using 2°C/min heating rate and by a Mettler Toledo Typus TGA/SDTA 851e in a nitrogen atmosphere (50 mL/min) and a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC823e under an argon atmosphere at a heating rate of 10 °C/min. Matrix-assisted laser desorption ionization high resolution mass spectra (MALDI HRMS) were recorded on a MS Bruker Reflex 2 (Bruker Daltonik GmbH) using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix. UV-vis absorption spectra were recorded in quartz cuvettes with 1 cm diameter with a Perkin Elmer Lambda 19 spectrometer. Emission spectra were recorded with a Perkin Elmer LS 55 also in quartz cuvettes with 1 cm diameter. Film emission spectra were recorded on a Perkin Elmer fluorescent Spectrometer FL 6500. Cyclic voltammetry was performed by using a computer controlled Autolab PGSTAT30 potentiostat with a three electrode single-compartment cell. A platinum working electrode, a platinum wire counter electrode, and a Ag/AgCl reference

electrode were used. All potentials were measured versus the redox couple ferrocene/ferricenium ( $\text{Fc}/\text{Fc}^+$ ) as internal standard. Surface images of photoactive layers were recorded with an atomic force microscope (Multi-Mode V AFM, Bruker). The microscope was operated in air at room temperature in the tapping mode using commercial silicon tips at resonance frequency of 200-400 kHz and spring constants of ca.  $50 \text{ Nm}^{-1}$ . The images were analysed with the help of WSxM software.<sup>6</sup> GIXRD measurements were carried out on using a Bruker D8 diffractometer with a fixed incoming angle of  $0.2^\circ$ . TEM images were recorded on a Zeiss EM 109 transmission electron microscope using acceleration voltage of 80 kV.

### 1.1. Device fabrication of organic solar cells

Indium tin oxide (ITO) patterned glass substrates ( $15 \Omega \text{ cm}^{-2}$ , from Naranjo Substrates) were precleaned with acetone, Mucosol soap solution, and isopropanol, before treated in a UV-ozone cleaner for 30 min. PEDOT:PSS (Clevios P, VP.AI 4038 aqueous solution from Heraeus) was spin-coated at 3000 rpm to obtain thin films of 20-30 nm thickness. The active layer solutions (conc. 15 mg/mL in chloroform) were deposited by spin-coating at various spin speeds. Thin films of LiF (0.7 nm) and aluminum (100-120 nm) were deposited by high-vacuum evaporation at pressures below  $3 \times 10^{-6}$  mbar (Nano 36, from Kurt J. Lesker Co.). Solvent vapour annealing (SVA) was performed by a literature known procedure.<sup>7</sup> One substrate contained four photoactive areas of 0.09 and 0.16  $\text{cm}^2$ .  $J$ - $V$ -characteristics of the prepared devices were obtained by using a solar simulator (class AAA, AM 1.5G,  $10 \text{ mW cm}^{-2}$  from Oriel Instruments). Apart from lithium fluoride and aluminium deposition, processing and characterization of the solar cells were performed under ambient conditions. The EQE was measured under monochromatic light from a 300 W Xenon lamp in combination with a monochromator (Oriel, Cornerstone 260), modulated with a mechanical chopper. The response was recorded as the voltage over  $220 \Omega$  resistance using a lock-in amplifier (Merlin 70104). A calibrated Si-cell was used as a reference (Newport 70356\_70316NS). Active layer thickness was determined by profilometer Veeco Dektak 150 High Performance Surface Profiler.

### 1.2. Device fabrication of organic field-effect transistors

Substrates with pre-patterned interdigitated gold electrodes in bottom-contact bottom-gate configuration (IPMS Fraunhofer Institute) were used. They consisted of a  $n^{++}$ -Si layer with 230 nm of thermally grown  $\text{SiO}_2$  as the gate dielectric (15 nF capacitance) All solutions, samples and devices were prepared and measured in a  $\text{N}_2$ -filled glovebox to avoid oxidative doping of the materials and to ensure reproducibility of the experiments. Solutions were prepared and deposited following the same procedure as for the solar cells. The  $\text{CS}_2$  treatment was also performed following the procedure for the solar cells.

Device characteristics were measured by contacting source, drain, and gate electrodes and applying different voltages to obtain  $I_{\text{DS}}-V_{\text{GS}}$  graphs. Measurements were performed using Keithley devices and the software Labtracer. Each  $I_{\text{DS}}-V_{\text{GS}}$  transfer curve was constructed by sweeping the gate voltages from -60V to +60V (n-type charge transport) or +60 V to -60 V (p-type charge transport), with one

measurement every 2 V. The drain voltage was either +60 V (n-type charge transport) or -60 V (p-type charge transport).  $I_{DS}$  was measured each time. Using the software Origin pro 8.0, transfer curves were plotted and fitted to extract the value of the mobility. The output curves were used to extract the value of the  $I_{on}/I_{off}$  ratio by dividing the value of the observed current in the saturation regime when the transistor is 'on' ( $I_{DS,max}$ ) by the value of the current when the transistor is 'off' ( $I_{DS,min}$ ). Experimental data were analyzed using the standard field-effect transistor equations for the saturation regime.

### 1.3. Synthesis

*4-{4-[(Triisopropylsilyl)oxy]butyl}-4H-dithieno[3,2-b:2',3'-d]pyrrole (3)*. Dibrominated bithiophene **1** (55.0 mg, 0.17 mmol), tris(dibenzylideneacetone)dipalladium(0) ( $Pd_2dba_3$ ) (6.20 mg, 0.01 mmol), 2,2-bis(diphenylphosphino)-1,1'-binaphtyl (BINAP) (10.7 mg, 0.02 mmol) and sodium tert-butoxide (50.0 mg, 0.51 mmol) were dissolved in 3 mL dry toluene and degassed with argon for 30 min. Subsequently, TIPS-protected amine **2** (50 mg, 0.2 mmol) was added and the reaction mixture degassed for 10 min. The reaction mixture was stirred at 110 °C for 24 h, poured into petroleum ether, and the organic phase was washed three times with saturated sodium chloride solution and dried over  $MgSO_4$  before evaporating the solvent. Purification was carried out by column chromatography over silica using petroleum ether as eluent. 65.0 mg (0.16 mmol, 96 % yield) of dithienopyrrole **3** was isolated as yellow oil.  $^1H$ -NMR (400 MHz,  $CDCl_3$ , 25 °C)  $\delta$  [ppm] = 7.13 (d,  $^3J_{HH} = 5.6$  Hz, 2 H, DTP- $\beta$ -H), 7.02 (d,  $^3J_{HH} = 5.6$  Hz, 2 H, DTP- $\alpha$ -H), 4.27 (t,  $^3J_{HH} = 6.4$  Hz, 2 H,  $-CH_2-$ ), 3.69 (t,  $^3J_{HH} = 6.4$  Hz, 2 H,  $-CH_2-$ ), 2.04-1.96 (m, 2 H,  $-CH_2-$ ), 1.59-1.52 (m, 2 H,  $-CH_2-$ ), 1.10-1.01 (m, 21 H, -TIPS-H).  $^{13}C$ -NMR (101 MHz,  $CDCl_3$ , 25 °C)  $\delta$  [ppm] = 141.66, 119.52, 111.41, 107.73, 59.48, 44.13, 27.06, 23.75, 14.77, 8.69. HRMS (APCI-FTICR)  $m/z$ :  $[M]^+$  calculated for  $C_{21}H_{33}NOS_2Si$ : 407.17728; measured: 407.17781 ( $\delta m/m = 1.20$  ppm).

*4-{2-[(Triisopropylsilyl)oxy]butyl}-2,6-bis(trimethylstannyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (4)*. Dithienopyrrole **3** (190 mg, 0.47 mmol) was dissolved in 10 mL dry THF and cooled to -78 °C. After adding *n*-BuLi (0.64 mL, 1.03 mmol, 1.6 M in *n*-hexane) dropwise over 15 minutes, the mixture was stirred at the same temperature for 1 h, followed by stirring at 0 °C for an additional hour. After cooling the reaction to -78 °C again, trimethyltin chloride (205 mg, 1.03 mmol) dissolved in 2 mL THF was added, and the reaction mixture was stirred for additional 3 h. The cold mixture was poured into water and extracted with dichloromethane. The organic phase was washed with water three times, dried over  $Na_2SO_4$ , and evaporated in vacuum. Dithienopyrrole **4** (334 mg, 0.46 mmol, 97 % yield) was obtained as a brown solid and used without further purification.  $^1H$ -NMR (400 MHz,  $CDCl_3$ , 25 °C)  $\delta$  [ppm] = 7.01 (s, 2H, DTP- $\beta$ -H), 4.24 (t,  $^3J_{HH} = 7.2$  Hz, 2H,  $-CH_2-$ ), 3.70 (t,  $^3J_{HH} = 6.1$  Hz, 2H,  $-CH_2-$ ), 2.05-1.97 (m, 2H,  $-CH_2-$ ), 1.63-1.55 (m, 2H,  $-CH_2-$ ), 1.07-1.01 (m, 21H, -TIPS-H), 0.42-0.37 (m, 18H, Sn-( $CH_3$ )<sub>3</sub>).  $^{13}C$ -NMR (101 MHz,  $CDCl_3$ , 25 °C)  $\delta$  [ppm] =  $\delta$  147.75, 135.50, 120.08,

117.81, 62.66, 47.35, 30.19, 26.92, 17.84, 11.84, -8.23. HRMS (MALDI-FTICR)  $m/z$ :  $[M]^+$  calculated for  $C_{27}H_{49}NOS_2SiSn_2$ : 735.10688; measured: 735.10778 ( $\delta m/m = 1.22$  ppm).

*5',5'''-{4-{6-[(Triisopropylsilyl)oxy]butyl}}-(4H-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl)bis(3,4'-dihexyl[2,2'-bithiophene]-5-carbaldehyde (6)*. Dithienopyrrole **4** (240 mg, 0.33 mmol) and 5'-bromo-3,4'-dihexyl-2,2'-bithiophene-5-aldehyde **5** (318 mg, 0.72 mmol) were dissolved in 10 mL dry DMF and purged with argon for 30 min.  $[Pd(PPh_3)_4]$  (19 mg, 16  $\mu$ mol) were added and the reaction mixture was stirred for 24 h. The mixture was poured into methanol and the resulting precipitate was filtered and washed with methanol. The crude product was purified by column chromatography over flash silica in petroleum ether/dichloromethane (30:70) as eluent and by size exclusion chromatography (SEC) with dichloromethane as eluent to obtain dialdehyde **6** (255 mg, 0.23 mmol, 69 % yield) as a deep red solid. Mp. 58-62 °C.  $^1H$ -NMR (400 MHz,  $CDCl_3$ , 25 °C)  $\delta$  [ppm] = 9.82 (s, 2H, CHO), 7.59 (s, 2H, Th- $\beta$ -H), 7.15 (s, 2H, Th- $\beta$ -H), 7.08 (s, 2H, DTP- $\beta$ -H), 4.28 (t,  $^3J_{HH} = 5.7$  Hz, 2H,  $-CH_2-$ ), 3.71 (t,  $^3J_{HH} = 5.7$  Hz, 2H,  $-CH_2-$ ), 2.84 (m, 2H,  $-CH_2-$ ), 2.11-1.98 (m, 8H,  $-CH_2-$ ), 1.78-1.56 (m, 8H,  $-CH_2-$ ), 1.51-1.30 (m, 24H,  $-CH_2-$ ), 1.11-0.99 (m, 21H, -TIPS-H), 0.95-0.86 (m, 12H,  $-CH_3$ )  $^{13}C$ -NMR (125 MHz,  $C_2D_2Cl_4$ , 80 °C, UDEFT)  $\delta$  [ppm] = 181.87, 144.56, 140.35, 140.18, 138.27, 130.29, 115.62, 110.01, 109.90, 62.59, 47.48, 31.42, 31.35, 30.33, 30.22, 29.95, 29.27, 28.94, 28.84, 26.80, 22.31, 22.28, 17.84, 13.71, 12.02. HRMS (MALDI-FTICR)  $m/z$ :  $[M]^+$  calculated for  $C_{63}H_{89}NO_3S_6Si$ : 1127.49360; measured: 1127.49238 ( $\delta m/m = 1.08$ ).

*5',5'''-[4-(4-Hydroxybutyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl]bis(3,4'-dihexyl[2,2'-bithiophene]-5-carbaldehyde (7)*. TIPS-protected dialdehyde **6** (180 mg, 0.16 mmol) and tetrabutylammonium fluoride (840 mg, 3.2 mmol) were dissolved in dry dichloromethane and stirred at 25 °C for 21 days. Subsequently, the organic phase was washed three times with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Column chromatography over silica using dichloromethane/ethyl acetate (95:5) as eluent gave alcohol **7** (124 mg, 0.13 mmol, 80 % yield) as a deep red solid. Mp. 89-91 °C.  $^1H$ -NMR (500 MHz,  $C_2D_2Cl_4$ , 80 °C)  $\delta$  [ppm] = 9.72 (s, 2H, -CHO), 7.54 (s, 2H, Th- $\beta$ -H), 7.09 (s, 2H, Th- $\beta$ -H), 7.03 (s, 2H, DTP- $\beta$ -H), 4.21 (m, 2H,  $-CH_2-$ ), 3.70-3.47 (m, 2H,  $-CH_2-$ ), 2.77 (m, 8H,  $-CH_2-$ ), 2.04-1.91 (m, 2H,  $-CH_2-$ ), 1.72-1.48 (m, 10H,  $-CH_2-$ ), 1.45-1.15 (m, 24H,  $-CH_2-$ ), 0.99-0.95 (m, 12H,  $-CH_3$ ).  $^{13}C$  NMR (125 MHz,  $C_2D_2Cl_4$ , 80 °C, UDEFT)  $\delta$  [ppm] = 181.91, 144.54, 140.90, 140.39, 140.17, 138.31, 134.07, 133.30, 132.66, 130.31, 115.68, 109.87, 62.05, 60.03, 47.26, 31.41, 31.34, 30.22, 29.95, 29.88, 29.27, 28.95, 28.84, 26.72, 22.32, 22.28, 17.53, 14.02, 13.72, 12.32. HRMS (MALDI-FTICR)  $m/z$ :  $[M]^+$  calculated for  $C_{54}H_{69}NO_3S_6$ : 971.35962; measured: 971.35590 ( $\delta m/m = 0.38$  ppm).

*2,2'-{[(4-(4-Hydroxybutyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole-2,6-diyl)bis(3,4'-dihexyl-[2,2'-bithien]-5',5'-diyl)]bis(methaneylylidene)}dimalononitrile (8)*. Dialdehyde **7** (100 mg, 0.10 mmol), malononitrile (136 mg, 2.06 mmol), and ammonium acetate (318 mg, 4.11 mmol) were dissolved in 30 mL dichloroethane and stirred 48 h at 80 °C. Subsequently, the mixture was diluted with dichloromethane and

washed four times with saturated sodium chloride solution. Column chromatography over silica using dichloromethane/ethyl acetate (95:5) as eluent and precipitation in MeOH gave 87 mg (0.08 mmol, 79 %) of metallic black solid. Mp. (DSC) 212 °C. <sup>1</sup>H-NMR (500 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 80 °C) δ [ppm] = 7.62 (s, 2H, DCV-H), 7.52 (s, 2H, Th-β-H), 7.19 (s, 2H, Th-β-H), 7.11 (s, 2H, DTP-β-H), 4.25 (t, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 2H, -CH<sub>2</sub>-), 3.65 (t, <sup>3</sup>J<sub>HH</sub> = 5.8 Hz, 2H, -CH<sub>2</sub>-), 2.83 (dd, <sup>3</sup>J<sub>HH</sub> = 15.6, <sup>4</sup>J<sub>HH</sub> = 8.2 Hz, 8H, -CH<sub>2</sub>-), 2.02 (dt, <sup>3</sup>J<sub>HH</sub> = 14.7, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2H, -CH<sub>2</sub>-), 1.78-1.54 (m, 8H, -CH<sub>2</sub>-), 1.48-1.28 (m, 26H, -CH<sub>2</sub>-), 1.18 (s, 1H, -OH), 0.92-0.83 (m, 12H, -CH<sub>3</sub>). <sup>13</sup>C-NMR (125 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 80 °C, UDEFT) δ [ppm] = 149.79, 145.22, 144.13, 141.57, 141.34, 141.00, 136.03, 133.64, 132.46, 132.10, 131.71, 116.45, 114.62, 113.72, 110.47, 62.47, 47.72, 31.81, 31.72, 30.64, 30.28, 30.15, 29.74, 29.53, 29.39, 29.23, 27.16, 22.74, 22.68, 14.10. HRMS (MALDI-FTICR) *m/z*: [M]<sup>+</sup> calculated for C<sub>60</sub>H<sub>69</sub>N<sub>5</sub>O<sub>6</sub>: 1067.38209; measured: 1067.38016 (δ*m/m* = 1.80 ppm).

[6,6]-Phenyl-C<sub>61</sub>-butyric acid-(2-{2,6-bis[5'-(2,2-dicyanovinyl)-3',4-dihexyl[2,2'-bithien]-5-yl]-4H-dithieno[3,2-b:2',3'-d]pyrrol-4-yl}butyl)ester (**1**). To a mixture of 20 mL dry chlorobenzene and 10 mL carbon disulfide PC<sub>61</sub>BA (40.0 mg, 0.04 mmol), oligomer **8** (48.0 mg, 0.04 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (10.0 mg, 0.05 mmol), 4-(dimethylamino)pyridine (7.00 mg, 0.05 mmol), and triethylamine (5 μL, 0.05 mmol) were added and the reaction mixture was stirred for 4 d at 25 °C. After removal of carbon disulfide, the mixture was diluted with chloroform and washed three times with saturated sodium chloride solution. Column chromatography over silica using toluene as eluent and precipitation from methanol gave dyad **1** (60.0 mg, 0.03 mmol, 69% yield) as a dark blue solid. Melting range: 105-115 °C. <sup>1</sup>H-NMR (500 MHz C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 80 °C) δ [ppm] = 7.81 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2H, Ph(o)-H), 7.63 (s, 2H, DCV-H), 7.52 (s, 2H, Th-β-H), 7.42 (m, 2H, Ph(m)-H), 7.38 (m, 1H, Ph(p)-H), 7.20 (s, 2H, Th-β-H), 7.09 (s, 2H, DTP-β-H), 4.22 (t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, 2H, -CH<sub>2</sub>-), 4.12 (t, <sup>3</sup>J<sub>HH</sub> = 6.3 Hz, 2H, -CH<sub>2</sub>-), 2.97-2.89 (m, 10H, -CH<sub>2</sub>-), 2.48 (t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 2H, -CH<sub>2</sub>-), 2.17-2.08 (m, 2H, -CH<sub>2</sub>-), 2.03-1.93 (m, 2H, -CH<sub>2</sub>-), 1.76-1.63 (m, 10H, -CH<sub>2</sub>-), 1.48-1.27 (m, 24H, -CH<sub>2</sub>-), 0.99-0.95 (m, 12H, -CH<sub>3</sub>). <sup>13</sup>C-NMR (125 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>, 80 °C, UDEFT) δ [ppm] = 172.85, 149.77, 148.99, 147.98, 145.92, 145.39, 145.35, 145.26, 145.18, 145.14, 144.99, 144.80, 144.69, 144.50, 144.17, 144.08, 143.94, 143.87, 143.16, 143.05, 142.34, 142.31, 142.27, 141.59, 141.33, 141.10, 141.04, 140.90, 138.13, 137.80, 137.00, 135.95, 133.81, 132.49, 132.21, 132.17, 131.71, 128.61, 128.41, 116.70, 114.62, 113.71, 110.38, 90.15, 90.13, 80.40, 76.39, 63.93, 52.12, 47.50, 34.30, 33.88, 31.83, 31.74, 30.65, 30.13, 29.78, 29.57, 29.43, 29.25, 27.29, 26.63, 22.76, 22.73, 22.70, 14.16. HRMS (MALDI-FTICR) *m/z*: [M]<sup>+</sup> calculated for C<sub>131</sub>H<sub>79</sub>N<sub>5</sub>O<sub>2</sub>S<sub>6</sub>: 1946.45580; measured: 1946.45791 (δ*m/m* = 1.08 ppm).

## 2. $^1\text{H}$ -, $^{13}\text{C}$ -NMR spectra

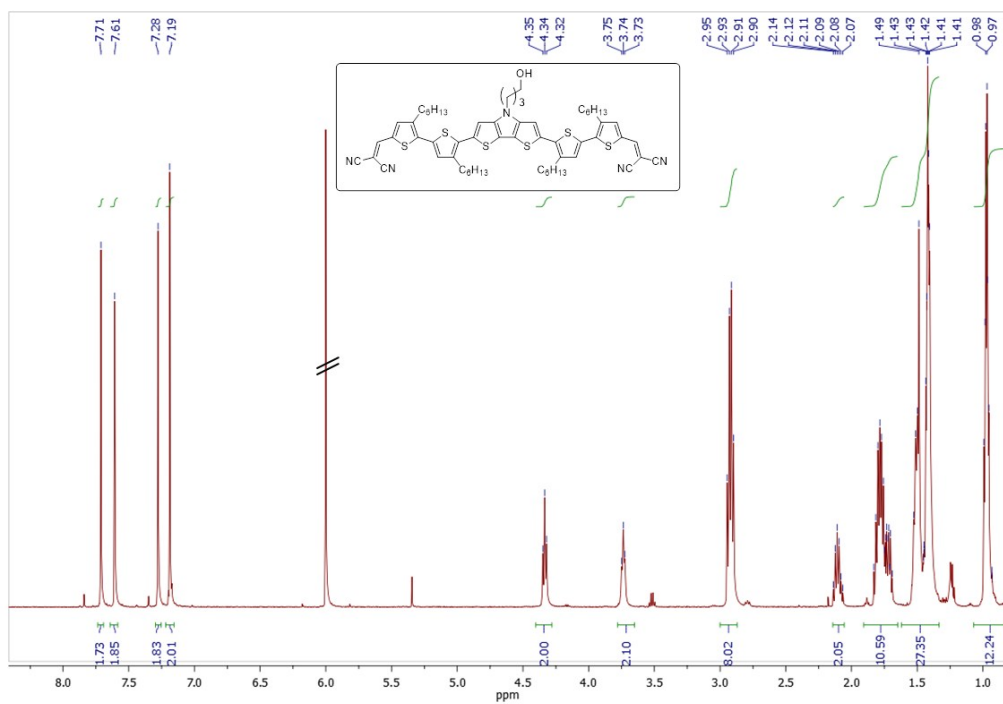


Figure S1  $^1\text{H}$ -NMR of co-oligomer **8** in  $\text{TCE-d}_2$ .

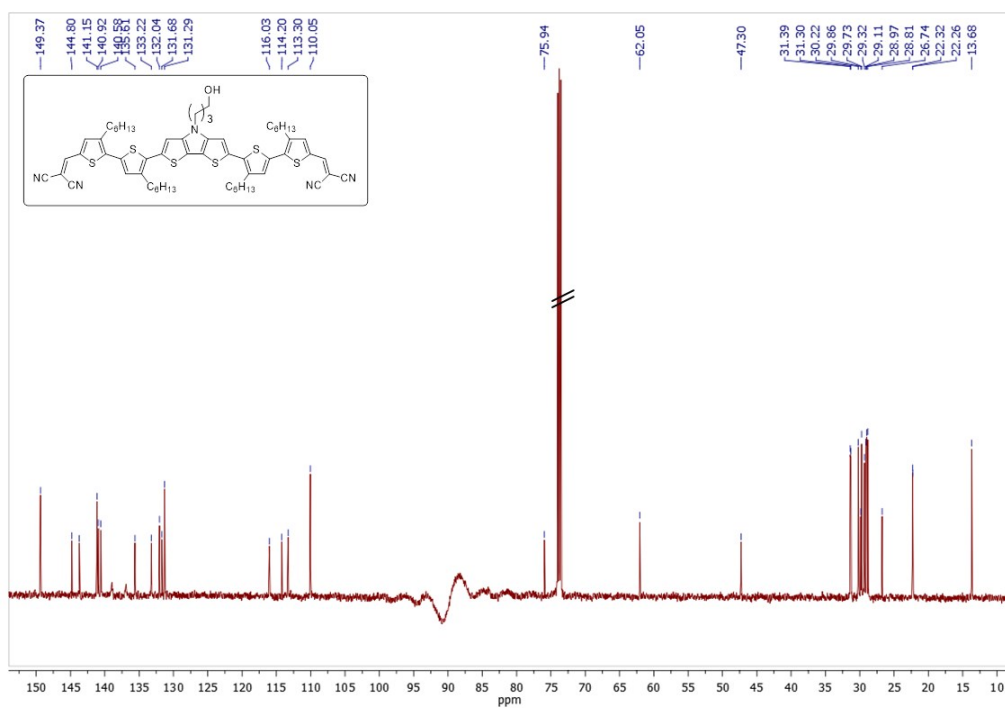


Figure S2  $^{13}\text{C}$ -NMR of co-oligomer **8** in  $\text{TCE-d}_2$ .

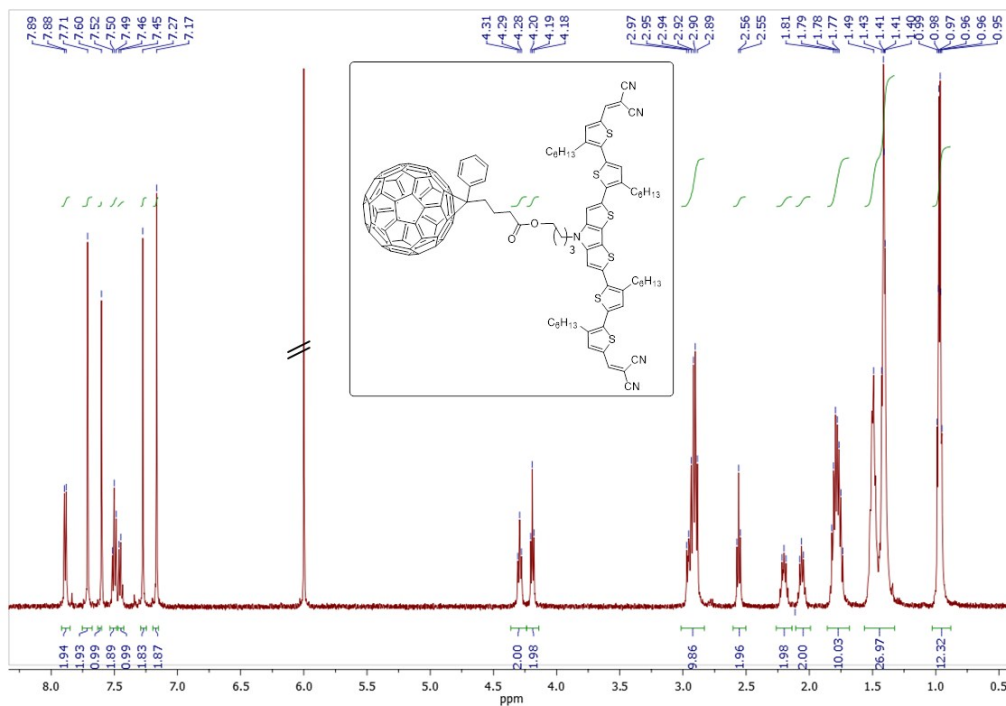


Figure S3 <sup>1</sup>H-NMR of dyad 1 in TCE-d<sup>2</sup>.

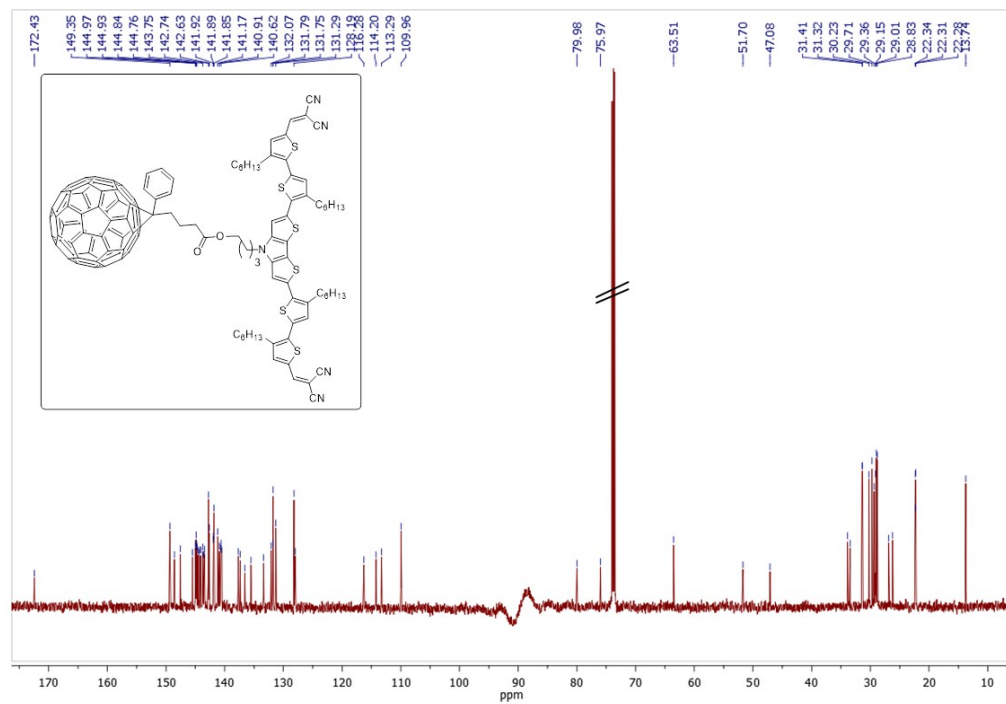
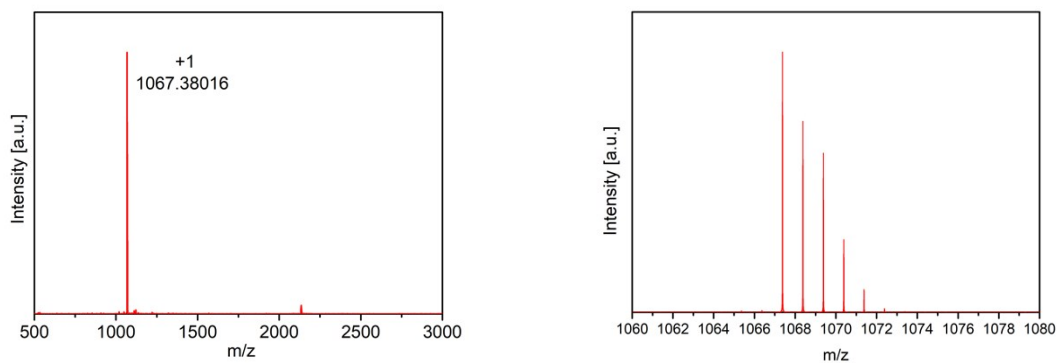


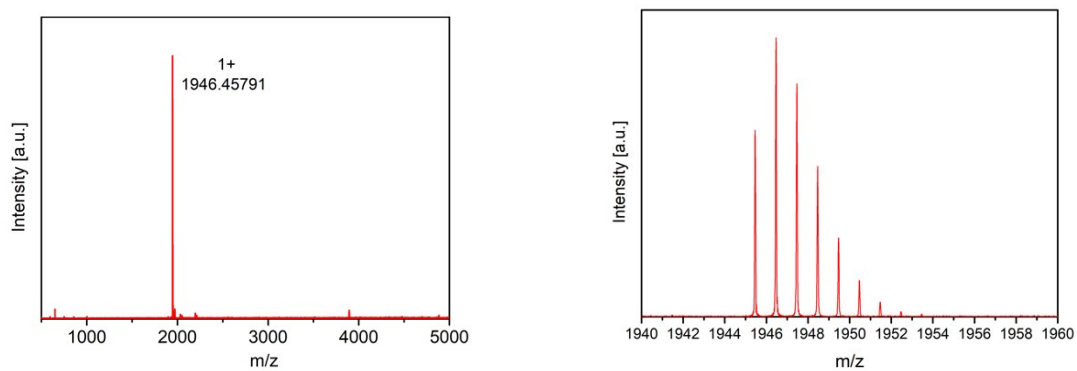
Figure S4 <sup>13</sup>C-NMR of dyad 1 in TCE-d<sup>2</sup>.



### 3. HRMS (MALDI-FTICR)

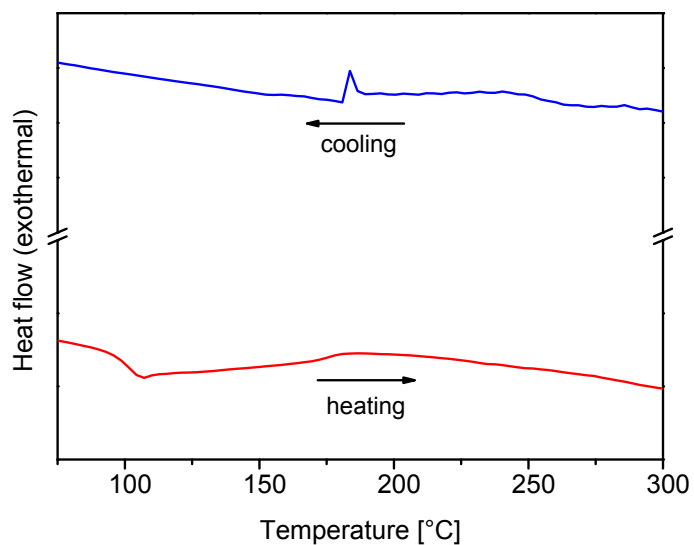


**Figure S5** HRMS (MALDI-FTICR, matrix: DCTB) of co-oligomer **8** (left) and isotopic pattern (right).

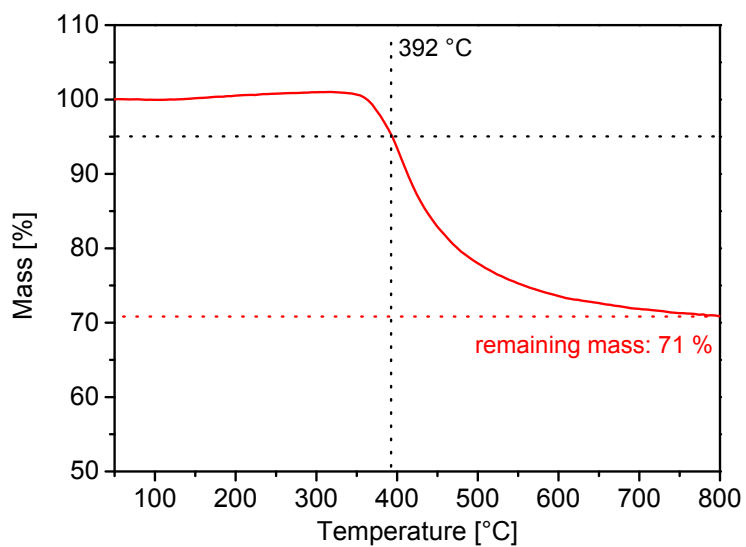


**Figure S6** HRMS (MALDI-FTICR, matrix: DCTB) of dyad **1** (left) and isotopic pattern (right).

#### 4. Thermal characterization of dyad **1** with DSC and TGA

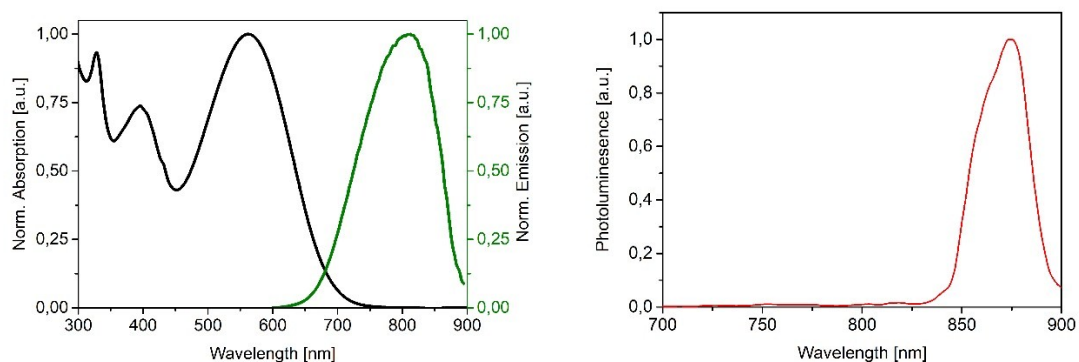


**Figure S7** DSC traces of dyad **1**, (red) heating, (blue) cooling, 10°C/min.

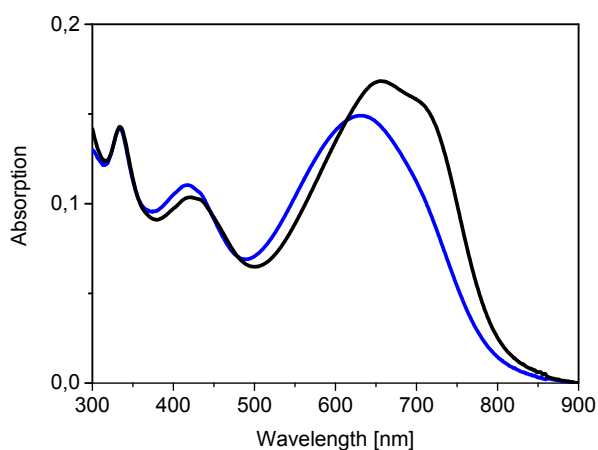


**Figure S8** TGA trace of dyad **1** (recorded at 10°C/min).

## 5. Optical characterization of dyad 1



**Figure S9** UV-vis absorption spectrum (black) and emission spectrum (green) of dyad **1** measured in dichloromethane solution (left); emission spectrum of a film of dyad **1** coated on glass from chloroform solution. Excitation wavelength: 580 nm (right).



**Fig. S10** Relative absorption of the photoactive layer with dyad **1** in SMOSCs before (blue) and after SVA (black).

## 6. Optimization of dyad 1 in single material organic solar cells

**Table S1** Photovoltaic parameters of dyad 1 for varying spin speeds with and without SVA with tetrahydrofuran (THF).

Spin speed	Layer thickness [nm]	SVA	$V_{oc}$ [V]	$J_{sc}$ [mA/cm <sup>2</sup> ]	FF	PCE [%]
1000 rpm	110	-	0.84±0.01 (0.85)	4.70±0.15 (4.88)	0.31±0.01 (0.31)	1.24±0.05 (1.29)
1000 rpm	110	THF/30 s	0.78±0.01 (0.79)	8.38±0.09 (8.51)	0.35±0.01 (0.35)	2.27±0.02 (2.30)
2000 rpm	85	THF/30 s	0.80±0.01 (0.81)	8.48±0.19 (8.70)	0.40±0.01 (0.41)	<b>2.73±0.06</b> <b>(2.82)</b>
3000 rpm	75	THF/30 s	0.80±0.01 (0.81)	7.25±0.29 (7.32)	0.43±0.01 (0.43)	2.45±0.11 (2.60)

Average value for 4 devices ± standard deviation, (best value); device architecture: glass/ITO/PEDOT:PSS/dyad 1/LiF/Al; spin-coated from chloroform solutions (c = 15 mg/mL) at r.t.

**Table S2** Photovoltaic parameters of dyad 1 with and without SVA with carbon disulphide (CS<sub>2</sub>).

SVA	$V_{oc}$ [V]	$J_{sc}$ [mA/cm <sup>2</sup> ]	FF	PCE [%]
-	0.86±0.01 (0.86)	5.38±0.23 (5.55)	0.35±0.01 (0.35)	1.60±0.06 (1.66)
CS <sub>2</sub> /20 s	0.79±0.01 (0.80)	8.78±0.27 (9.07)	0.42±0.01 (0.43)	<b>2.95±0.09</b> <b>(3.07)</b>
CS <sub>2</sub> /30 s	0.80±0.01 (0.81)	8.39±0.26 (8.64)	0.41±0.01 (0.41)	2.74±0.08 (2.80)

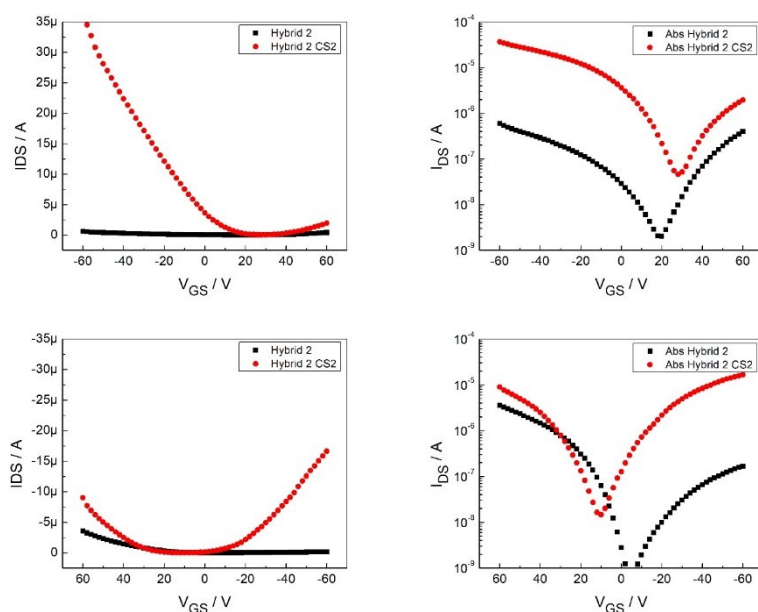
Average value for 4 devices ± standard deviation, (best value); device architecture: glass/ITO/PEDOT:PSS/dyad 1/LiF/Al; spin-coated from chloroform solutions (c = 15 mg/mL) at r.t. with 1500 rpm.

**Table S3** Photovoltaic parameters of dyad 1 with and without SVA with chloroform (CF).

SVA	$V_{oc}$ [V]	$J_{sc}$ [mA/cm <sup>2</sup> ]	FF	PCE [%]
-	0.86±0.01 (0.86)	5.38±0.23 (5.55)	0.35±0.01 (0.35)	1.60±0.06 (1.66)
CF/15 s	0.83±0.01 (0.83)	7.78±0.09 (8.02)	0.42±0.01 (0.42)	2.70±0.08 (2.79)
CF/20 s	0.83±0.01 (0.83)	8.63±0.15 (8.72)	0.43±0.01 (0.44)	3.09±0.04 (3.11)
CF/25 s	0.82±0.01 (0.83)	9.17±0.06 (9.21)	0.45±0.01 (0.45)	<b>3.35±0.02</b> <b>(3.39)</b>
CF/40 s	0.80±0.01 (0.81)	8.74±0.15 (8.84)	0.42±0.01 (0.42)	2.93±0.04 (2.96)

Average value for 4 devices ± standard deviation, (best value); device architecture: glass/ITO/PEDOT:PSS/dyad 1/LiF/Al; spin-coated from chloroform solutions (c = 15 mg/mL) at r.t. with 1500 rpm.

## 7. Electrical characterization of dyad 1 organic field-effect transistors



**Figure S11.** Transfer curves of transistors ( $L = 20 \mu\text{m}$ ) produced from D-A dyad **1** prior and after  $\text{CS}_2$  treatment at (a,b)  $V_{\text{DS}} = +60 \text{ V}$  and (c-d)  $V_{\text{DS}} = -60 \text{ V}$ . [ $L = 5 \mu\text{m}$ ,  $W = 10 \text{ nm}$ ,  $C = 15 \text{ nF cm}^{-2}$ ]. The scales on the voltage and current axes are the same in all graphs for the sake of comparison.

## Mobility measurements in organic field-effect transistors with dyad 1

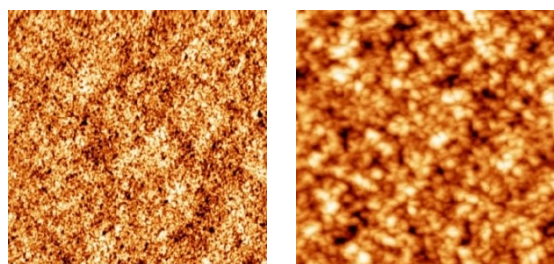
**Table S4** Electrical characteristics of dyad **1** field-effect transistors prior to SVA with carbon disulfide. Average saturation regime field-effect mobility for holes ( $\mu_{\text{p}}$ ) and electrons ( $\mu_{\text{n}}$ ) and threshold voltage ( $V_{\text{th}}$ ) of the devices prior to SVA.

	SVA	$\mu_{\text{n, sat}} \times 10^{-5}$ [ $\text{cm}^2/\text{Vs}$ ]	$V_{\text{th}}$ (electrons) [V]	$\mu_{\text{p, sat}} \times 10^{-5}$ [ $\text{cm}^2/\text{Vs}$ ]	$V_{\text{th}}$ (holes) [V]
Dyad <b>1</b>	-	$2.86 \pm 0.94$	$23 \pm 3$	$0.47 \pm 0.09$	$-6 \pm 3$
Dyad <b>1</b>	$\text{CS}_2$ 20 s	$7.76 \pm 3.14$	$30 \pm 4$	$26.30 \pm 2.99$	$7 \pm 4$

Average values for 4 devices  $\pm$  standard deviation (best value); two with channel length  $L=5 \mu\text{m}$  and two with  $L=10 \mu\text{m}$ .

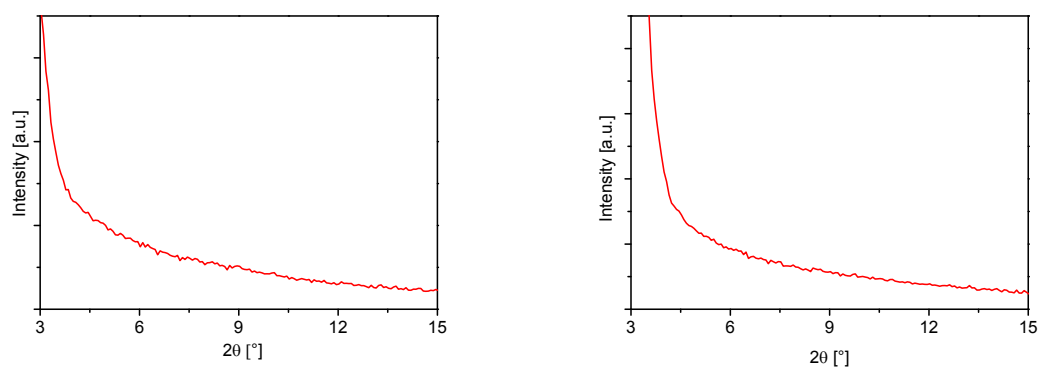
## 8. Morphological characterization of dyad **1**

### Atomic force microscopy (AFM)



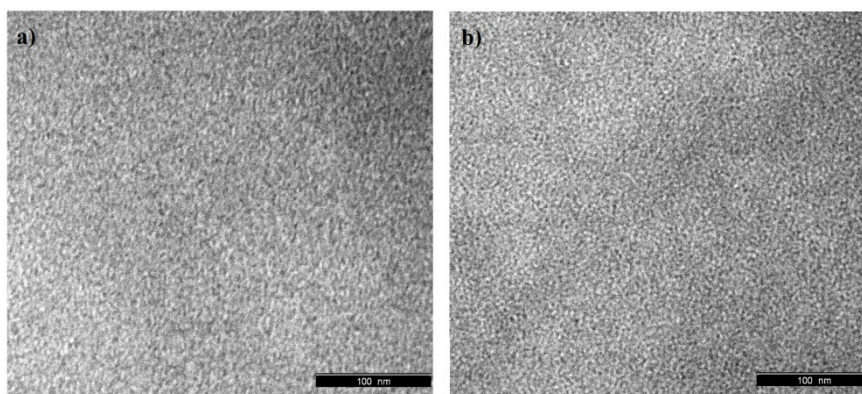
**Fig. S12** AFM topography images ( $1 \times 1 \mu\text{m}^2$ ) of photoactive layers of dyad **1** before ( $\Delta z=2\text{nm}$ ) (left) and after SVA (CF, 25 s) ( $\Delta z=5\text{nm}$ ) (right).

### Grazing incidence X-ray diffraction (GIXRD)



**Fig. S13** GIXRD measurements were performed at an incidence angle of  $0.2^\circ$  for films of dyad **1** spin-coated on PEDOT:PSS coated substrates, as cast (left), after SVA (30 s, chloroform) (right).

### Transmission electron microscopy (TEM)



**Fig. S14** TEM images were recorded using 80 KV acceleration voltage on a Zeiss EM 109 transmission electron microscope. Films of dyad **1** spin-coated on PEDOT:PSS samples prepared by float-coating on Cu grids; as cast (left), after SVA (30 s, chloroform) (right).

## 9. Notes and references

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