Molecular Oligothiophene– Fullerene Dyad Reaching Over 5% Efficiency in Single-Material Organic Solar Cells

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1. Introduction

Single-material organic solar cells (SMOSCs) came into focus again, because the photoactive molecules and materials have been vastly improved in recent time.[1] The promise of facilitated cell fabrication by deposition of only one sole photoactive component leading to high thermal and light stability and therefore long-lived solar cells, renders SMOSCs to attractive candidates for technological production of large-scale organic solar cells.[2–9] Typically, polymeric or oligomeric materials comprising covalently linked electron-rich donor (D) and electron-deficient acceptor (A) units are developed. In most examples D and A are connected by flexible insulating linkers of various lengths corresponding to a molecular bulk heterojunction model, whereas only few have rigid π-conjugated linkers or are directly connected.[3] Among the ambipolar D–A copolymers, structurally challenging “double cable” polymers with high synthetic complexity[2–5] very recently showed significantly improved power conversion efficiencies (PCE) to over 8.4% in SMOSCs. In these materials, a lamellar phase-separation of D and A units is typically achieved at higher temperatures (up to 230 °C) resulting in solar cells with high thermal and light stability.[1c,5–8] Currently, these results have been outperformed by random D–A block copolymers[6–8] reaching a PCE of 8.6%[7] and even very promising 11.3%[8] catching the 10% technological barrier for industrial applications.[1c,10]

It is well accepted that structurally defined semiconducting molecular materials have particular advantages such as monodispersity and reproducibility over polydisperse polymers, which contain chain length distributions and defects to a certain extent.[11] Various oligomeric D–A dyads and triads have been prepared and optimized for SMOSCs over time,[1] and general structural concepts include: 1) D and A are directly connected in an “in-chain” approach leading to fully π-conjugated alternating D–A systems. The best result in this category was achieved with oligofluorene-alt-bithiopheneperylenediimide dyads, which after post-treatment with solvent vapor annealing (SVA) gave device performances of up to 1.75% PCE;[12] 2) D and A are linearly linked via flexible linkers in the so-called “side-chain” approach in an 1:1 or 1:2 ratio, whereby an oligothiophene–PC71BM fullerene dyad recently described by Min et al. reached a PCE of 3.22% in SMOSCs;[13] 3) Similar to the subunits in “double cable” polymers, oligomeric donor backbones were substituted at the central unit with pending PC61BM or PC71BM fullerenes in a “T-shaped” fashion, but typically reached efficiencies of only below 2%.[1] An improved performance of up to 2.5% PCE was obtained by the attachment of non-fullerene perylene diimide side chains to a conjugated oligomer backbone comprising diketopyrrolopyrrole and benzodithiophene units.[14] We recently could further improve the performance of SMOSCs in this category by developing ambipolar “T-shaped” D–A dyads 1–3 consisting of a dithienopyrrole...
(DTP)-based A–D–A-type oligomer as D and fullerene PC_{61}BM as A which were linked by a flexible alkyl ester chain with spacer lengths of 8–12 atoms. SMOSCs containing dyad 1 with the shortest spacer in the photoactive layer in a “normal” cell architecture reached PCEs of 4.26% after post-treatment with SVA which is the highest reported to date for molecular single materials. The rational molecular design and precise distance of the oligothiophene D and fullerene A resulted in strongly confined lamellae of nanoscopic dimensions allowing for crucial phase separation as important key to ambipolar charge transport and well performing and highly stable SMOSCs.\[9b\]

Herein, we now report the extension of our molecular design to D–A dyad 4, in which PC_{61}BM of formerly best performing dyad 1 is replaced by the larger and less symmetric PC_{71}BM as acceptor leading to substantially improved SMOSCs with over 5% efficiency and high short-circuit current density $J_{SC}$ of 13.56 mA cm$^{-2}$ after SVA. This improvement is due to increased spectral absorption of the films, more efficient charge generation, dissociation, and transport as well as reduced charge recombination. Analysis of the energy losses gave detailed information on radiative and nonradiative recombination.\[13,15\] Moreover, dyad 4-based SMOSCs showed excellent stability under continuous light exposure retaining 96% of the initial efficiency after 750 h (1 month).

2. Results and Discussion

2.1. Synthesis of D–A Dyad 4

The synthetic route to D–A dyad 4 is shown in Scheme 1 and detailed synthetic procedures are given in the Supporting Information. Hydroxyethyl-substituted dialdehyde 1\[9b\] and fullerene carboxylic acid PC_{71}BA 2 were connected in a Steglich esterification furnishing D–A intermediate 3 in 74% yield. This was converted in a Knoevenagel condensation with malononitrile and ammonium acetate to targeted dicyanovinylene (DCV) end-capped dyad 4 in a yield of 90%. Oligomer 5 was accordingly synthesized as a reference molecule and mimics the donor subunit of dyad 4 (see the Supporting Information). The elaborated synthesis route over six reaction steps and starting from commercially available reagents delivered D–A dyad 4 in 36% overall yield which will allow for up-scaling. The structures of D–A systems 3, dyad 4, and reference 5 were confirmed by $^1$H- and $^{13}$C-NMR-spectroscopy (Figures S1–S3, Supporting Information) and high resolution mass spectra (HRMS) (Figures S4–S6, Supporting Information). Dyad 4 exhibited good thermal stability with degradation temperature $T_d > 395 \degree C$ (5% weight loss) which was determined by thermal gravimetric analysis (TGA) (Figure S7, Supporting Information). Differential scanning calorimetry (DSC) first heating thermogram revealed an endothermic peak at 123 $\degree C$ which we address to a glass transition temperature $T_g$ due to the mainly amorphous character of this type of dyad.\[9b\] The second DSC heating scan only revealed a (shallow) exotherm at 260 $\degree C$ which most probably arises from the PC_{71}BM side chains and reflects cold recrystallization.\[16\] This finding is in accordance with the corresponding scan of pure amorphous PC_{71}BM in which this transition is recovered (Figure S8, Supporting Information).

2.2. Optical and Redox Properties of D–A Dyad 4

The optical properties of well soluble D–A dyad 4 were investigated by UV–vis and fluorescence spectroscopy in dichloromethane (DCM) solutions (Figure 1, left) and in thin films before and after SVA (Figure 1, right). The data is compiled in Table 1 and compared to corresponding PC_{61}BM-dyad 1\[9b\] and to reference D 5 without pending fullerene unit. The absorption spectrum of dyad 4 (black curve) reflects a superimposition of the absorption of Dsubunit 5 (green curve) and A PC_{71}BM (red curve). The strongest main absorption band with a maximum

Scheme 1. Synthetic route for the preparation of dyad 4 and structure of reference donor 5.
at 552 nm is attributed to the π–π* (HOMO-LUMO) transition with charge-transfer (CT) character coming from the A–D–A structure of the D unit and is slightly blue shifted compared to PC\textsubscript{71}BM-dyad 1 (blue curve) and reference 5. The higher energy band at 400 nm comprises the characteristic pure D π–π* and \n\nπ–n* transitions and the weaker shoulders at 472 and 378 nm are assigned to the appended PC\textsubscript{71}BM. At the low energy side of the spectrum, the onset of absorption was found at 692 nm leading to an optical energy gap of 1.79 eV which is in accordance with those of dyad 1 and reference 5. For all three molecules, emission maxima were found in the regime of 812–814 nm and arise from the excitation of oligomeric D units.

UV-vis spectra of thin films of dyad 4, which were prepared by spin-coating of chloroform solutions on glass slides, were measured before and after SVA with carbon disulfide (CS\textsubscript{2}) (black curves) in comparison to the film spectra of dyad 1 (blue, dotted line) and after SVA (black, full line) in comparison to dyad 1 before (blue, dotted line) and after SVA (blue, full line) (right).

Table 1. Optical properties of dyad 4 in comparison to dyad 1,\textsuperscript{[9b]} donor reference 5, and PC\textsubscript{71}BM in dichloromethane solution and in thin films before and after SVA.

|       | \(\lambda_{\text{max}}^{\text{sol}}\) [nm]\textsuperscript{a} | \(\varepsilon\) [M\textsuperscript{-1} cm\textsuperscript{2} \text{mol}\textsuperscript{-1}] | \(\lambda_{\text{onset}}^{\text{sol}}\) [nm]\textsuperscript{a} | \(\lambda_{\text{em}}^{\text{sol}}\) [nm]\textsuperscript{a} | \(E_{\text{g}}^{\text{sol}}\) [eV]\textsuperscript{b} | \(\lambda_{\text{em}}^{\text{film}}\) [nm]\textsuperscript{c} | \(E_{\text{g}}^{\text{film}}\) [eV] | 
|-------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Dyad 4 | 552, 472 (sh), 400, 378 | 63 140 | 692 | 814 | 1.79 | 580, 410, 382 | 1.58 |
| Dyad 4 (SVA) | | | | | | | |
| Dyad 1 | 563, 395, 328 | 57 055 | 684 | 812 | 1.81 | 596, 408, 330 | 1.53 |
| Dyad 1 (SVA) | | | | | | | |
| PC\textsubscript{71}BM | 459, 372, 356 | 31 280 | 700 | | 1.77 | 473, 377 | 1.67 |
| 5 | 562, 400, 310 | 59 940 | 695 | 814 | 1.78 | 692, 641, 431 | 1.55 |

\textsuperscript{a}Measured in dichloromethane, maxima underlined; \textsuperscript{b}Thin films by spin-coating from chloroform solution on glass, maxima underlined; \textsuperscript{c}Taken from onset of absorption and calculated by \(E_{g} = 1240/\lambda\), sh = shoulder

Figure 1. Absorption (black, solid line) and emission spectrum (black, dotted line) of dyad 4, dyad 1 (blue), donor reference 5 (green), PC\textsubscript{71}BM (red), and measured in dichloromethane solution at room temperature (left). Absorption spectra of thin films of dyad 4 before (black, dotted line) and after SVA (blue, full line) in comparison to dyad 1 before (blue, dotted line) and after SVA (blue, full line) (right).
increased with respect to dyad 1 (Figure 2c, bottom, left). Concomitant with the optical data, dyad 4 should therefore represent a good candidate for application in SMOSCs.

### 2.3. Photovoltaic Data

The excellent solubility of dyad 4 in solvents such as chloroform (86 mg mL\(^{-1}\)), chlorobenzene, or \(\alpha\)-xylene allowed the preparation of defect-free thin films by spin-coating under ambient conditions. Sole photovoltaic SMOSCs layers were optimized using the “normal” architecture glass/ITO/PEDOT:PSS.dyad 4/LiF/Al in terms of processing solvent, SVA solvent and exposure time, concentration of the coating solution, thickness of the photoactive layer by spin-speed variation, and additives (Tables S2–S8, Supporting Information). For advanced investigations SMOSCs with the “inverted” device structure glass/ITO/ZnO/dyad 4/MoO\(_x\)/Ag were used and compared to dyad 1 in the same device architecture. The best performing SMOSCs were obtained by spin-coating a 15 mg mL\(^{-1}\) solution of dyads 4 and 1 in chloroform at a spin-speed of 1500 rpm at room temperature leading to film thicknesses of 100 \(\pm\) 5 nm and post-treatment of the films with 30 s of SVA in CS\(_2\) atmosphere (Table 2). 

### J–V-characteristics under 100 mW cm\(^{-2}\) simulated AM 1.5G illumination of the best performing SMOSC with dyad 4 as cast and after SVA are shown in Figure 2a and compared to the performance of PC\(_{71}\)BM-based dyad 1. Thus, SMOSCs containing dyad 4 clearly outperformed those with dyad 1 in the pristine and as well in the post-treated state showing improved PCE from 4.50% to 5.34% (SVA), respectively. The enhancement in

| D–A dyad | SVA solv. (time) | \(V_{OC} [\text{V}]\) | \(J_{SC} [\text{mA cm}^{-2}]\) | FF | PCE [%] | EQEmax [%] | \(J_{SC,SVA} [\text{mA cm}^{-2}]\) |
|----------|-----------------|-----------------|-----------------|-----|--------|---------|-----------------|
| Dyad 4   | –               | 0.87 \(\pm\) 0.01 (0.88) | 3.46 \(\pm\) 0.14 (3.56) | 0.31 \(\pm\) 0.01 (0.31) | 0.93 \(\pm\) 0.04 (0.97) | 17.2 (@ 530 nm) | 3.31 |
| Dyad 4   | CS\(_2\) (30 s) | 0.83 \(\pm\) 0.01 (0.83) | 13.20 \(\pm\) 0.25 (13.56) | 0.48 \(\pm\) 0.01 (0.48) | 5.20 \(\pm\) 0.09 (5.34) | 54.2 (@ 660 nm) | 12.31 |
| Dyad 1   | –               | 0.87 \(\pm\) 0.01 (0.88) | 3.41 \(\pm\) 0.14 (3.52) | 0.28 \(\pm\) 0.01 (0.28) | 0.83 \(\pm\) 0.03 (0.87) | 17.1 (@ 610 nm) | 3.37 |
| Dyad 1   | CS\(_2\) (30 s) | 0.85 \(\pm\) 0.01 (0.85) | 10.26 \(\pm\) 0.13 (10.81) | 0.48 \(\pm\) 0.01 (0.49) | 4.18 \(\pm\) 0.05 (4.50) | 52.7 (@ 660 nm) | 10.7 |

Average values for 15 devices \(\pm\) standard deviation (best value).
efficiency mainly arises from the substantially increased photocurrent density $J_{SC}$ of 13.56 mA cm$^{-2}$ in dyad 4 which is the highest value so far measured in oligomer-based SMOSCs.$^{[9,13]}$ The additional absorption of the pending PC$_{71}$BM compared to dyad 1 (Figure 1, right) contributes to this outstanding $J_{SC}$ and is well reflected in the EQE-spectra, in which dyad 4 showed an increased photon-to-charge carrier conversion of above 50% in the wavelength regime of 350–850 nm. A maximum EQE value of 54.2% is obtained at 660 nm, which is the highest for oligomer-based SMOSCs (Figure 2b).

At slightly lower open circuit voltage $V_{OC}$, the fill factor FF is identical for dyad 4 indicating a similar molecular organization and nanomorphology in the photoactive film.$^{[96]}$ The PCE above 5% obtained for dyad 4 outperforms several of the polymer-based SMOSCs$^{[1]}$ and represents a new best value for molecular materials which has been raised from recently 3.22%$^{[13]}$ to 4.26%$^{[9b]}$ and now to 5.34% by advancement of the D–A dyad structures (Figure 2d; and Table S13, Supporting Information).

### 2.4. Long-Term Stability of Dyad 4-Based SMOSCs

In order to further highlight the advantages of SMOSCs, especially for D–A oligomeric systems, we conducted illumination stability test of dyad 4 devices at room temperature in nitrogen atmosphere under continuous LED light exposure with an intensity of 100 mW cm$^{-2}$ (Figure S10, Supporting Information). Figure 3 exhibits the evolution of the photovoltaic parameters, in which the PCE showed a tiny decrease in the beginning and then stayed flat afterward, retaining 96% of the initial efficiency after 750 hours (1 month). $V_{OC}$ and FF stayed fairly stable over time, while the slight decrease of $J_{SC}$ is responsible for the total decrease, which we ascribe to the reorganization of fullerene aggregates and the contact with interface layers. This result is in accordance with the previous reported data for dyad 1, which also exhibited excellent illumination stability, indicating a potential generality in high illumination stability for SMOSCs based on D–A molecular systems.$^{[1c,9b]}

### 2.5. Photoluminescence (PL) and Time-Resolved Photoluminescence (TrPL) Analyses

To investigate the charge transfer (CT) behavior, photoluminescence (PL) and the time-resolved PL (TrPL) decay were measured accordingly. PL spectra of films are shown in Figure 4a. Apparently, both dyads 4 and 1 show significantly quenched PL emission compared to pure donor 5 and fullerenic acceptors, indicating efficient CT between the two moieties. Moreover, after SVA post-treatment, the emission is further quenched for both dyads 4 and 1 (Figure S11, Supporting Information). The results from PL quenching indicate effective exciton dissociation and CT. This emission quenching behavior was further precisely investigated through TrPL experiments (Figure 4b,c). For the films of pure donor 5 and fullerenic acceptors, PL intensity shows a triexponential decay behavior with a lifetime of 521.6 ps for D 5, and 973.1 and 721.1 ps for PC$_{71}$BM and PC$_{61}$BM, respectively (Table S9 and Figure S12, Supporting Information). Dyad 4 and 1 exhibited a faster decay than the pure D and A films. Particularly, the decay is even accelerated after SVA treatment (Table S9 and Figure S13, Supporting Information).

For the emission from the D segment, the lifetime of dyad 1 is shortened from 223.9 to 58.1 ps after SVA and the one of dyad 4 from 217.0 to 56.2 ps. For the emission from the A part, the difference in lifetime before and after SVA is less compared with the difference of emission from the D, whereby the lifetime of dyad 1 decreases from 37.6 to 34.2 ps and of dyad 4 from 37.1 to 31.9 ps. Compared to the A segment, this more significant change of lifetime for the D segment reveals that SVA treatment mainly contributes to the improvement of the D morphology, while the fullerenic acceptors are less influenced by SVA.$^{[96]}$ In particular, dyad 4 shows the fastest decay with a lifetime of 56.2 ps for the emission from the D segment and 31.9 ps for the emission from the A segment. This phenomenon indicates a significantly improved D packing after SVA post-treatment for dyad 4, where excitons generated in the D region are most efficiently dissociated at the D/A interface.

### 2.6. Energy-Loss Analyses

For the determination of the detailed energy loss, we first calculated the effective energy bandgaps ($E_g$) of dyad 4- and dyad 1-based devices by the method originally proposed by Rau et al. and recently extended by Almora et al. The detailed analysis is described in the Supporting Information (Figure S14 and Table S10, Supporting Information) and results in an identical bandgap value $E_g$ of 1.62 eV for dyad 1 and dyad 4.$^{[17]}$ In order to determine the origin of the voltage losses from the detailed balance theory, electroluminescence (EL) spectra, and Fourier transform photocurrent spectroscopy–external quantum efficiency (FTPS-EQE) measurements were carried out on dyad 4 and dyad 1 devices.$^{[18–20]}$ It is well

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*Figure 3.* Illumination stability of SMOSCs based on dyad 4 at room temperature under continuous LED light illumination with the intensity of 100 mW cm$^{-2}$.
accepted that the three sources of energy loss ($E_{\text{loss}}$) obey the following equation \cite{21,22}

$$E_{\text{loss}} = (E_{\text{pp}} - qE_{\text{CT}}) + (q\Delta V_{\text{OC,rad}}) + (q\Delta V_{\text{OC,irr}}) = \Delta E_1 + \Delta E_2 + \Delta E_3$$

(1)

The calculated energy loss from bandgap to $V_{\text{OC}}$ is similar for SMOSCs with dyad 1 (0.77 eV) and with dyad 4 (0.79 eV).

The CT state energies ($E_{\text{CT}}$) were estimated by simultaneously fitting EL and EQE$_{\text{PV}}$ according to the literature.\cite{23,24}

As shown in Figure 4d,e, the $E_{\text{CT}}$ values of dyad 4- and dyad 1-based SMOSCs were determined to be 1.29 and 1.22 eV. The related losses are calculated via $\Delta E_1 = E_g - qE_{\text{CT}}$. The different $E_{\text{CT}}$ values reflect a weakening of the CT state ($\Delta E_1$) for dyad 1-based SMOSCs (0.33 eV) compared to those of dyad 4 (0.40 eV). The energetic position and the intensity of the CT states of dyad 1- and 4-based SMOSCs are counterbalancing the sub-bandgap losses and result in similar $V_{\text{OC,rad}}$ values (the detailed analysis is described in the Supporting Information), which were calculated to 1.19 and 1.20 V (Table 3, detailed calculation procedure in the Supporting Information). The third
loss due to nonradiative charge carrier recombination, \( \Delta E_1 = q\Delta V_{OC,rad} \) reflects the difference between \( qV_{OC,rad} \) and the measured \( qV_{OC} \) under AM 1.5G simulated solar spectrum. Dyad 4-based SMOSCs exhibited slightly higher \( \Delta E_1 \) value than dyad 1, which could be responsible for the slightly lower \( V_{OC} \) from dyad 4. Further research is required to better understand the nature of the nonradiative recombination losses. Gernate recombination is expected to be more dominant in SMOSCs because of their inherent intimate mixture and has to be studied in detail.

### 2.7. Charge Recombination and Transport

In order to display other factors contributing to the large difference in \( J_{SC} \), we investigated the charge recombination process in both SMOSCs based on dyad 4 and dyad 1. \( J_{ph} - V_{eff} \) characteristics was first measured and is shown in Figure 5a. Under high reverse bias, the saturated current density \( J_{ph, sat} \) was determined and the maximum charge generation rate \( (G_{max}) \) was calculated accordingly. As listed in Table S11 (Supporting Information), dyad 4 showed an increased \( G_{max} \) of 1.14 \( \times 10^{18} \) m\(^{-3} \) s\(^{-1} \) compared to 7.89 \( \times 10^{17} \) m\(^{-3} \) s\(^{-1} \) for dyad 1 which is as well enhanced compared to the device without SVA post-treatment (Figure S15, Supporting Information). Light intensity \( (P_{light}) \) dependent photovoltaic performance was also measured for dyad 4 and dyad 1. From the \( J_{SC} - P_{light} \) plots as shown in Figure S16 (Supporting Information), dyad 4- and dyad 1-based SMOSCs showed almost unity dependence of \( J_{SC} \) on \( P_{light} \), indicating negligible effect from 2nd order recombination. From the \( V_{OC} - P_{light} \) plots (Figure 5b), we observed a dependence of \( V_{OC} \) on \( P_{light} \) for dyad 4- and 1-based SMOSCs with a slope of 1.21 or 1.49 kT q\(^{-1} \), reflecting the existence of both, 2nd order recombination and trap-assisted recombination.\[^{[12]}\] Additionally, charge transport was as well investigated for dyad 4 and 1. From the space charge limited current (SCLC) measurements (Figures S17, S18, and Table S12, Supporting Information), dyad 4 showed slightly higher mobilities for holes and electrons (7.58 \( \times 10^{-3} \) cm\(^2 \) V\(^{-1} \) s\(^{-1} \), holes; 1.31 \( \times 10^{-4} \) cm\(^2 \) V\(^{-1} \) s\(^{-1} \), electrons) compared to dyad 1 (6.48 \( \times 10^{-5} \) cm\(^2 \) V\(^{-1} \) s\(^{-1} \), holes; 8.64 \( \times 10^{-5} \) cm\(^2 \) V\(^{-1} \) s\(^{-1} \), electrons).\[^{[25]}\]

### 2.8. Film Morphology

In order to obtain information on the impact of SVA on the nanomorphology of the photoactive layer of dyad 4, we investigated the surface by means of tapping mode atomic force microscopy (AFM). Topography images for the as-cast films revealed a tightly packed morphology with smooth surface comprising statistically distributed small holes (\( d = 25–70 \) nm, \( h = 2–10 \) nm) (Figure S19, left, Supporting Information). After SVA, a morphological change is visible, whereby diameter and height of the holes are reduced \( (d = 25–60 \) nm, \( h = 2–4 \) nm) and roughness slightly increased \( (0.7–1.1 \) nm) (Figure S19, right, Supporting Information). Corresponding phase images in both cases lacked relevant contrast suggesting that phase separation should be smaller than the AFM-resolution of 15 nm. In the case of dyad 1, AFM topography images revealed finest morphology with small structural features, which were slightly growing after SVA.

We attempted the investigation of the inner film morphology by grazing-incidence wide-angle X-ray scattering (GIWAXS) of

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### Table 3. Summary of measured and calculated parameters from FTPS-EQE and EL.

|        | \( E_T \) [eV] | \( V_{OC} \) [V] | \( E_{loss} = E_T - qV_{OC} \) [eV] | \( E_{CT} \) [eV] | \( \Delta E_1 = E_T - E_{CT} \) [eV] | \( V_{OC,rad} \) [V] | \( \Delta E_2 = q\Delta V_{OC,rad} \) | \( V_{CT} - qV_{OC,rad} \) | \( \Delta E_3 = \Delta V_{OC} \) [eV] |
|--------|--------------|----------------|---------------------------------|----------------|---------------------------------|----------------|-------------------------------|----------------|------------------|
| dyad 1 | 1.62         | 0.85           | 0.77                            | 1.29           | 0.33                            | 1.19           | 0.10                          | 0.40            | 0.34              |
| dyad 4 | 1.62         | 0.83           | 0.79                            | 1.22           | 0.40                            | 1.20           | 0.02                          | 0.37            |                  |

\( E_T \) was determined by the method reported by Almora; \( V_{OC} \) was measured under a solar simulator; \( \Delta V_{OC,rad} \) is the radiative limit to \( V_{OC} \), measured and calculated using FTPS; \( \Delta V_{OC} \) is the voltage loss due to non-radiative recombination.
samples of dyad 4 before and after SVA. The results confirm that the films also after SVA are highly disordered and amorphous due to diffuse reflections in the GIWAXS patterns. According to the 2D images and the z- and y-cuts, unfortunately, not a ring nor other hints for slight π–π stacking of the donor subunits could be identified in each of the samples. In comparison to the symmetrical C₆₀ moiety in dyad 1, which showed weak ordering of the D units in films after SVA, the larger and unsymmetrical C₇₀ moiety in dyad 4 obviously prevents better self-organization. However, these subtle differences did not lead to significant changes in the fill factor FF of SMOSCs, which practically was the same for both derivatives (vide supra).

3. Conclusion

We have extended our molecular design concept for structurally defined, covalently linked D–A dyads by preparing ambipolar derivative 4, in which a p-type oligothiophene D and a n-type PC₇₁BM fullerene A unit are linked by a flexible alkyl ester chain in a “T-shaped” fashion. The exchange of the pending PC₆₀BM unit in the previously reported dyad 1 for the larger and less symmetrical PC₇₁BM in 4 led to fairly enhanced photovoltaic performance in SMOSCs. The rise to the highest PCE of 5.34% for molecular materials (see Figure 2) mainly derives from a substantially increased photocurrent density J_SC of 13.56 mA cm⁻². The additional absorption of the pending PC₇₁BM contributes to the outstanding J_SC, which outperforms several of the polymer-based SMOSCs, and is well reflected in the increased photon-to-carrier conversion with EQE values over 50% over the visible region (see Figure 2). Moreover, dyad 4-based SMOSCs showed a promising long-term stability under continuous light exposure by retaining 96% of the initial efficiency after 750 h (1 month). With respect to the fundamental photophysics and charge carrier dynamics, SMOSCs based on dyad 4 not only showed an increased efficiency of exciton splitting to overcome the exciton binding energy, but also improved charge transport and led to less trap-assisted recombination of holes and electrons compared to corresponding dyad 1. The detailed energy losses were calculated and analyzed taking the energetics of the CT-states and band gaps of both dyads into account.

The semiquantitative structure–property–device performance relationships obtained in this investigation for our oligomeric D–A dyads will help in joint efforts to further upgrade the rational development of photoactive single materials by chemists and of SMOSC devices by physicists and engineers. Starting points would be to further widen and intensify the absorption range of D–A systems into the NIR by tuning the molecular structure. It is expected that advanced photophysics and a further increase of J_SC could be obtained. A further key step, which however is still difficult to achieve, is the control of the structurally imprinted self-organization behavior of the dyads to form less amorphous photoactive supramolecular nanostructures with optimally segregated and oriented D and A domains allowing for ameliorated charge separation and transport.

Despite the advantageous performance of highly optimized binary or ternary bulk-heterojunction solar cells, the plausible simplified concept of SMOSCs might evolve to a follow-up technology for practical application in the near future, if their recently achieved continuously improving photovoltaic performance will persist.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
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Data Availability Statement
Research data are not shared.

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