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A–D–A-type S,N-Heteropentacenes: Next-Generation Molecular Donor Materials for Efficient Vacuum-Processed Organic Solar Cells

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Conjugated oligomers, often referred to as "small molecules", come more and more into focus as organic semiconductors in organic solar cells (OSC).^[1] Not only do the power conversion efficiencies (PCE), up to 9%, reach those of corresponding polymer solar cells,^[2–4] but also high reproducibility is achieved due to the defined molecular structure.^[5] Besides common processing from solution, oligomers furthermore allow processing by evaporation, which leads to highly controlled and well-defined layers of high purity.^[6] An additional advantage is that vacuum techniques are solvent-free, while especially the frequently used chlorinated solvents are a critical technical issue in solution-processing and printing of organic solar cells.^[7]

In this respect, so-called A–D–A oligothiophenes (A = acceptor, D = donor) turned out to be a very promising and successful class of compounds. Starting from an initial efficiency of 3.4% for single-junction solar cells comprising a 2,2-dicyanovinyl (DCV)-capped quinquethiophene (DCV5T-Bu) as p-type and fullerene C₆₀ as n-type semiconductor,^[8] by optimization of the molecular structure and device preparation, a PCE of 6.9% was recently achieved with a similar methylated derivative (DCV5T-Me).^[9] Vacuum-processing allows the construction of complex multilayer device structures and PCEs of tandem cells were continuously improved to 10.7% by Heliatek GmbH.^[10] This culminated in a certified record efficiency of 12.0% on 1.1 cm² by a triple cell construction as well using A–D–A oligothiophene/C₆₀ subcells.^[11]

In the search for even stronger absorbers, which at the same time have good charge-transport properties, are thermally stable, and sublime nearly without residue, we very recently introduced fused thiophene-pyrrol-based *S*,*N*-heteroacenes and their acceptor-capped derivatives as next-generation A–D–A donor molecules.^[12] Corresponding DCV-substituted *S*,*N*-heterohexacene DCV-SN6 showed very intense optical transitions and exhibited high p-channel charge-carrier mobilities caused

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by an extended band-like π -conjugated backbone comprising substantial quinoidal character and bond-length equalization in the ground state. In this novel class of potential donor materials for OSCs, we were able to combine the favorable properties of oligothiophenes, which exhibit increased stability due to a low-lying highest occupied molecular orbitial (HOMO) energy level, and of oligoacenes, which typically show high charge-transport mobilities due to a planar, rigid, and highly conjugated backbone.^[13]

In this contribution, we report synthesis, characterization, and photovoltaic properties of a novel series of DCV-capped S,N-heteropentacenes (DCV-SN5) 1-3, in which the substituent at the nitrogen atoms is varied (Figure 1). In comparison to the nonfused terthiophene parent oligomer DCV3T 4, which has a rather modest performance in solar cells,^[14] a strong redshift and intensification of the absorption by keeping suitable energy levels of the frontier orbitals were obtained. In vacuumprocessed single-junction m-i-p solar cells,^[15] efficiencies as high as 6.5% for propyl derivative 1 as donor and fullerene C_{60} as acceptor were achieved after optimization of the processing parameters during device fabrication. Characterization of the photoactive blends (oligomers $1-3/C_{60}$) by atomic force microscopy (AFM) gave a clear correlation of the phase separation with the trend seen in the photovoltaic parameters, which eventually depend on the molecular structure: 1 (propyl) >2 (hexyl) >>3 (tolyl).

The synthesis of novel A-D-A-type fused S,N-heteropentacenes 1-3 is outlined in Scheme 1. The crucial building block 3,3',3",4'-tetrabromo-2,2':5',2"-terthiophene 7 was synthesized in a 78% yield by a Negishi-type cross-coupling reaction of tetrabromothiophene 5 and (3-bromothien-2-yl)zinc(II) chloride 6 in the presence of dichloro[1,1'-bis(diphenylphosphino)ferrocene]palladium (Pd(dppf)Cl₂) as catalyst.^[16] The next step was a fourfold Buchwald-Hartwig amination reaction of terthiophene 7 with different amines in the presence of Pd(dba)₂ as the Pd source, dppf as ligand, and sodium *tert*-butoxide as base. The S,N-heteropentacenes 8-10 were obtained in good yields of 50–60%. In the next step, fused heteroaromatics 8--10 were converted into corresponding dialdehydes 11-13 by Vilsmeier-Haack formylation in 75-85% yield after column chromatography. Subsequent Knoevenagel condensation with malonitrile gave DCV end-capped target S,N-heteropentacenes 1-3 in excellent yields of 80-88%.

The thermal properties of 1–3 were investigated using differential scanning calorimetry (DSC) (Figure S1, Supporting



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Figure 1. Molecular structures of acceptor-substituted *S*,*N*-heteropentacenes **1–3** in comparison to non-fused parent oligothiophene DCV3T **4**.

Information) and thermogravimetric analysis (TGA) (Figure S2, Supporting Information). In comparison to the parent DCV3T 4 (265 °C),^[17] ring-fusion increased the melting point to 414 °C for 1, to 296 °C for 2, and to 395 °C for 3 indicating strong intermolecular interactions in the solid state. All three derivatives displayed high thermal stability with an onset of the decomposition temperature (T_d) at around 400 °C for 1, 353 °C for 2, 392 °C for 3, respectively, as confirmed by TGA.

Single crystals of DCV-SN5 **1** obtained by fractionated sublimation crystallized in the monoclinic space group P 2₁/n with four equivalent molecules in the unit cell arranging in antiparallel pairs with a 2-fold screw axis symmetry (*a* = 7.34121(11), *b* = 27.6849(4), *c* = 12.5274(2) Å; α = 90.00°, β = 103.8281°(15), γ = 90.00°) (**Figure 2**c). Bond lengths, selected angles, and torsion angles are compiled in Table S1 in the Supporting Information. The two alkyl chains of each molecule



are directed out of plane in the opposite direction of the planar conjugated backbone (Figure 2a,b and Figure S3, Supporting Information). The conjugated backbone of DCV-SN5 1 exhibits bond-length equilibration with an extremely small averaged difference of 0.01 Å (Table S1, Supporting Information). DCV-SN5 1 arranges in perfectly antiparallel stacked columns of pairs of molecules separated by a distance of 9 Å (Figure 2b). Strong π - π interactions at distances of 3.45 Å and 3.493 Å stabilize the columns (Figure 2b, and Table S2, Supporting Information). Perpendicular to the -101 plane, DCV-SN5 1 interacts with four other molecules via various cyano groups, which come close to vinylic or heteroaromatic hydrogens or to sulphur atoms (Figure 2d (green and red lines), Table S3, Supporting Information).

The absorption spectra of DCV-SN5 derivatives **1–3** in dichloromethane solution and in thin films are shown in **Figure 3** and compared to the parent oligomer DCV3T **4**. All the data are summarized in **Table 1**. The fluorescence spectra of **1–3** and DCV3T **4** are shown in the supporting information (Figure S5, Supporting Information).

We will discuss the general trends of the optoelectronic properties of DCV-SN5 1–3 in comparison to DCV3T 4 which can be derived from the data and give an indication on the influence of the planarization and rigidification in the fused SN5-systems. First of all, the maximum absorption and fluorescence of 1–3 in solution and absorption in thin films is strongly shifted to longer wavelengths and the molar extinction coefficient is increased by a factor of 1.8–2.3 as compared to DCV3T 4. At the same time, the optical gap decreased. The influence of the rigidification of the conjugated π -system in 1–3 can as well be seen in the large decrease of the Stokes shift compared to 4. Within the series of the fused DCV-SN5 1–3, there are small differences in the optical data of 1 and 2 compared to tolyl derivative 3 which for 3 indicate a distorsion of the bulky aromatic



Scheme 1. Synthesis of acceptor-substituted S,N-heteropentacenes 1–3.



Figure 2. Single-crystal X-ray structure analysis of DCV-SN5 1, individual molecule on the $(-12\ 10\ 10)$ plane (a) and packing arrangement in columns of pairs (b). The packing in the unit cell (c) and intramolecular short contacts between the adjacent individual molecules in layered packing motif viewed from the direction normal (d) and parallel (e) to the $(-1\ 0\ 1)$ plane.

substituents on the nitogen with respect to the conjugated SN5-backbone. In thin films, the absorbance of DCV-SN5 2 decreased by a factor of about 20% compared to 1 and 3 which



Figure 3. UV-vis spectra of DCV-SN5 **1-3** and parent oligomer DCV3T **4** in (a) dichloromethane solution at 25 °C and in (b) 30 nm thick films deposited by vacuum sublimation on glass substrates. The film spectrum of the frequently used zinc phthalocyanine $(ZnPc)^{[18]}$ is shown for comparison.

is ascribed to the presence of insulating hexyl substituents. Furthermore, it should be noted that in comparison to the frequently used ZnPc^[18] the film spectra of DCV-SN5 derivatives showed significant spectral broadening and strong increase in the absorbance and therefore could act as better light harvesters (Figure 3b).

The redox properties of 1-4 were determined by cyclic voltammetry in a dichloromethane/tetrabutyl ammonium hexafluorophosphate (0.1 M) electrolyte and the potentials were referenced against the redox couple ferrocene/ferricenium (Fc/Fc⁺), which was set to -5.1 eV vs vacuum^[19] in order to consequently calculate the frontier orbital levels. The data are summarized in Table 1 and representative CVs shown in Figure S6 in the Supporting Information. The trends seen in the optical measurement are continued and fused 1-3 showed a much lower first oxidation potential and therefore a destabilized HOMO compared to parent 4. The first reduction is at more negative potentials for the former series and the LUMOs are slightly stabilized, in total however, the electrochemical gap is diminished in agreement with the optical data. Still the HOMO energy levels of 1-3 lie sufficiently low to assure high open circuit voltages (V_{OC}) in bulk heterojunction solar cells and the LUMOs are sufficiently high to provide efficient electron transfer to the LUMO of the acceptor C_{60} (≈ -4.1 eV) used in the solar cells.^[20]

We performed quantum chemical DFT calculations on the fused DCV-SN5 1-3 in comparison to parent DCV3T 4 in order to see the influence of the rigidification on the electron density distribution in the respective systems. The reproduction of the frontier orbitals of DCV-SN5 1 and DCV3T 4 are shown in Figure 4. In contrast to the nonfused system, the electron density distribution in the HOMO of the fused system showed a noticeable contribution of the S and N heteroatoms.^[12,17] Furthermore, a continuous electron density is visible in the conjugated π -system in contrast to the classical nodal HOMO distribution of nonfused DCV3T 4 (Figure 4, bottom). In both cases, the LUMOs exhibited the classical quinoidal character with the electron density extended to the acceptor groups (Figure 4, top). The first electronic transition, which is calculated to be predominantly HOMO \rightarrow LUMO revealed stronger oscillator strenght for DCV-SN5 1 (f = 2.1) compared with non-fused 4 (f = 1.7). High values of the state dipoles evidence the CT-character of the transitions.

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Table 1. Optical and electrochemical properties of S,N-heteropentacenes 1–3 and DCV3T 4.^[17]

Oligomer	λ _{abs} sol [nm]	е [L mol ⁻¹ ст ⁻¹]	Eg ^{opt} sol ^{a)} [eV]	λ _{em} sol [nm]	Stokes shift [cm ⁻¹]	λ _{abs} film [nm]	E _g ^{opt} film ^{a)} [eV]	E ⁰ _{ox1} [V]	E ⁰ _{ox2} [V]	E ⁰ _{red1} [V]	HOMO ^{b)} [eV]	LUMO ^{b)} [eV]	E _g ^{CVc)} [eV]
1	582	140 000	1.99	616	714	595, 637	1.69	0.61	1.22	-1.43	-5.64	-3.78	1.86
2	582	139 100	2.01	612	579	594, 630	1.73	0.62	1.23	-1.50	-5.65	-3.79	1.86
3	575	108 800	2.04	605	691	579, 624	1.75	0.67	1.25	-1.57	-5.70	-3.79	1.91
4	495	59 300	2.20	564	1047	528, 574	1.85	1.06	-	-1.25	-6.09	-3.90	2.19

^{a)}Estimated using the onset of the UV-vis spectra, $E_g^{opt} = 1240/\lambda_{onset}$; ^{b)}Estimated from the onset of the respective redox waves, Fc/Fc⁺ value set to -5.1 eV vs vacuum; ^{c)}Calculated from $E_g = E_{LUMO} - E_{HOMO}$.



Figure 4. Representative HOMO/LUMO electron-density distribution of DCV-SN5 propyl derivative 1 and DCV3T 4 as reference.

In order to understand the influence of the substituents at the amino groups in DCV-SN5 1-3, bulk heterojunction solar cells with m-i-p-type (metal-intrinsic-p-doped) device architecture^[6,15] were prepared by vacuum deposition. The DCV-SN5 1-3 were used as the donor (D) and C_{60} as the acceptor (A) of the bulk heterojunction. The layer sequence in the device consisted of ITO/C₆₀ (15 nm)/DCV-SN5 1-3: C₆₀ (20 nm)/BPAPF (10 nm)/BPAPF:NDP9 (45 nm, 10 wt%)/NDP9 (1 nm)/Au (50 nm). The D:A ratio was 1:1 by volume and the two materials were coevaporated at a substrate temperature of 90 °C, which is important for the crystalline growth of the blend layer and enhanced fill factors.^[21] The BPAPF p-doped with NDP9 (10 wt%) was used as the hole transport layer (HTL), on top of which another 1 nm thick layer of NDP9 was deposited to facilitate charge extraction. The undoped BPAPF layer was introduced to avoid direct contact between the active layer and the doped BPAPF layer that otherwise could lead to quenching of excitons by the dopants.^[22] The *I-V* characteristics of the solar cells are shown in Figure 5a and summarized in Table 2. Corresponding EQE-spectra are depicted in Figure 5b.

All the solar cells showed high open-circuit voltages (V_{OC}) of around 0.95 V. These values are due to the low-lying HOMOs and typical for DCV-substituted oligothiophenes.^[8,17] With respect to the other photovoltaic parameters, the short-circuit current density (J_{SC}), fill factor (FF), saturation, EQE, and series resistance (R_S), the alkylated derivatives 1 and 2 clearly outperformed arylated DCV-SN5 3 which as well reflects the findings for the optoelectronic properties. The results were further supported by characterization of the photoactive blend layer by AFM. In total, a very good efficiency of 5.6% was found for propyl derivative 1, followed by the hexylated 2 (3.7%), and by

far lowest for the tolyl counterpart (0.7%). The reasonable values indicate that excitons are efficiently separated at the D-A interface and readily transported through the bulk. The saturation (defined as $J(-1 \text{ V})/J_{SC}$) close to unity, i.e., a weak voltage bias dependence of the current in reverse direction, determined for the alkyl derivatives 1 and 2 indicates that excitons are efficiently separated at the D-A interface and readily transported through the bulk.^[9,17] The FF, however, decreases from 0.70 for oligomer 1 to 0.49 for oligomer 2. This points to an impaired transport in the active mixed layer of 2 and C₆₀ leading to an increased voltage-dependent charge-carrier recombination between 0 V and V_{OC} . The longer alkyl chain length of 2 and, consequently, a higher intermolecular distance of donor molecules in the bulk could supply a possible explanation for this behaviour. In contrast to oligomers 1 and 2, the 3-based device showed a much lower performance. The low FF of 0.40 and the saturation of 1.59 suggest poor charge carrier transport. The $J_{\rm SC}$ is lower than in the 1- and 2-based devices despite similar chemical and energetic structures, as well as similar absorption. One possible explanation for this behaviour could be the trapping of charge carriers on the tolyl group leading to voltage independent recombination.

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At this point it is noteworthy, that parent, nonbridged oligothiophene DCV3T 4 and C_{60} did not lead to an efficient exciton separation into charge-carrier pairs at the interface because of the low HOMO offset between the two materials leading to a poor solar cell performance.^[14]

Because of the promising solar-cell performance of propyl derivative 1, we further optimized and investigated the influence of layer thickness and substrate heating temperature on the device performance. The data are summarized as well in Table 2 and shown in Figure S7 in the Supporting Information. Whereas only marginal changes in V_{OC} and fill factors were observed by increasing the photoactive layer thickness from 20 nm to 30 nm, the J_{SC} values were improved using the thicker layers. Irrespective of the film thickness, a continuous increase in the FF was observed with increasing substrate temperature from 70 °C to 90 °C reaching a maximum value of ca. 0.70, showing that exciton and charge separation efficiencies become less field-dependent with increasing temperature.

The best performance of a DCV-SN5 1:C₆₀ BHJ solar cell was finally achieved with a 30 nm active layer deposited at 90 °C substrate temperature exhibiting a mismatch-corrected $J_{\rm SC}$ value of 10.2 mA cm⁻², a $V_{\rm OC}$ of 0.92 V, and a FF of 0.69. This translates to 6.5% efficiency, which is among the best values for vacuum-processed single junction cells. It should be

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Figure 5. *J*–*V* characteristics (a) and EQE spectra (b) of m-i-p bulk-heterojunction solar cells prepared with DCV-SN5 **1–3** as donor and C_{60} as acceptor (active area 6.4 mm²).

noted that the devices were standard test structures for material comparison purposes without optimisation for microoptic cavity effects. Also, the Au counter electrode is suboptimal with respect to efficiency. The improvement in J_{SC} is in good agreement with the external quantum efficiency (EQE) measurements. The maximum EQE value for the most efficient device is close to 70% at 600 nm covering a broad spectral range from 300–700 nm. The improvement in device performance by increasing the substrate temperature is attributed to a change in the mixed layer morphology and resulting stronger phase separation induced by the applied substrate heating.^[21,23] All devices at higher temperature showed a low photocurrent saturation value of ca. 1.05 indicating efficient charge separation and extraction.^[17]

In this respect, the surface morphology of 20 nm thick 1-3:C60 photoactive blend layer prepared at 90 °C substrate temperature were investigated by atomic force microscopy (AFM) (Figure 6). Strong differences were seen for the DCV-SN5 derivatives 1-3 and are clearly a consequence of the different N-substitution. The surface of the 1:C₆₀ blend layer is uniformly composed of grains with a diameter of 30-50 nm at an average height of 14 nm (Figure 6a and Figure S8 in the Supporting Information) indicating better pathways for charge transport. The analysis of the corresponding phase images showed relevant phase shifts up to 74° (Figure 6d) and the histogram over several phase images discloses two well differentiated maxima of the phase-shift at 14° and 56°, which we attribute to the acceptor and donor homophases.^[24-26] The phase images revealed 20-30 nm isolated islands of the donor phase, which cover almost 25% of the surface area. The acceptor regions (low phase-shift) formed an interconnected network of thin fibrils whereas the mixed phase (ca. 50% of the surface area) appeared to surround the donor islands and is as well in contact with the acceptor network (Figure S9a, Supporting Information).

The surface of $2:C_{60}$ blend layers showed a less pronounced grain structure with a small average height of 2.6 nm (Figure 6b and Figure S8 in the Supporting Information). The phase images revealed a much finer structure, in which only very few and small islands of 1–10 nm (ca. 5% of the area) correspond to the donor phase and over 50% of the surface is covered by thick interconnected low phase-shift acceptor regions (Figure 6e and Figure S9b in the Supporting Information). The mixed areas in the case of $2:C_{60}$ are forming islands mostly in contact with the acceptor network.

Table 2. Photovoltaic parameters of BHJ-devices of DCV-SN5 derivatives 1-3:C₆₀ (blend ratio 1:1). Photovoltaic parameters of BHJ devices comprising $1:C_{60}$ (1:1) under variation of thickness and substrate temperature. Active area 6.4 mm².

DCV-SN5	Substrate temp. [°C]	Thickness [nm]	J _{sc} [mA cm ⁻²]	V _{oc} [V]	FF	PCE [%]	Sat. ^{a)}	EQE @ 600 nm [%]	R _s [Ω cm²]
3	90	20	1.94	0.95	0.40	0.7	1.59	17	19.6
2	90	20	7.97	0.95	0.49	3.7	1.09	62	4.3
1	90	20	8.43	0.94	0.70	5.6	1.05	63	3.0
1	80	20	8.53	0.96	0.61	5,0	1.06	58	3.2
1	70	20	8.60	0.94	0.36	2.9	1.20	62	4.1
1	90	30	10.20	0.92	0.69	6.5	1.05	70	3.1
1	80	30	9.60	0.95	0.59	5.4	1.06	66	3.6
1	70	30	9.60	0.94	0.42	3.8	1.13	72	4.0

^{a)}Defined as $J(-1 V)/J_{SC}$.



Figure 6. Tapping mode AFM topography (top) and phase (bottom) images ($1 \mu m \times 1 \mu m$) of blend films (1:1 w/w deposited at 90 °C substrate temperature) of **1**:C₆₀ (a,d), **2**:C₆₀ (b,e) and **3**:C₆₀ (c,f).

Finally, the AFM topography images of the surface of **3**:C₆₀ showed an almost featureless surface with few large aggregates (25–50 nm, height of up to 27 nm) (Figure 6c and Figure S8 in the Supporting Information). The very small phase shifts ($<5^{\circ}$) evidence the lack of phase separation in this blend (Figure 6f). Therefore, fast recombination of the generated charges should occur due to lack of percolation pathways, which is consistent with the low FF (0.40) and J_{SC} (2.8 mA cm⁻²) of the device.

In conclusion, we have reported the synthesis and characterization of novel acceptor-substituted S,N-heteropentacenes DCV-SN5 1-3 as next-generation A-D-A-type molecular donors for vacuum-processed organic solar cells. The three derivatives structurally differ by their alkyl substituent at the amino nitrogen (propyl/hexyl/tolyl). Single-crystal X-ray structure analysis of DCV-SN5 1 gave deeper insight into the specific intermolecular interactions and multiple nonbonding short contacts, which are responsible for the packing with strong π - π interaction and multidirectional electronic coupling. The optical and electrochemical properties have been studied to determine the optical absorption and energy levels. Single-junction m-i-p type solar cells fabricated with propyl derivative 1 as donor and fullerene C_{60} as acceptor gave the best PCE of 6.5% in the series due to enhanced photocurrent (J_{SC}) and fill factor (FF). The devices were optimized by varying substrate temperature and film thickness. The alkyl substitution in the series of DCV-SN5 1-3 strongly influences the device performance, which we attribute to the very different blend morphology and phase separation, as evidenced by AFM-techniques. Our investigation demonstrates that with this novel class of fused heterocycles, which combine increased stability of oligothiophenes with the rigid and extended π -conjugated backbone of oligoacenes, high-performance donor materials for organic solar cells have been designed and prepared. The transfer of the concept to larger *S*,*N*-heterooligoacenes and other ring-fused conjugated systems is under way in our laboratory.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author. The Supporting Information includes experimental details, synthesis, and analytical data of the oligomers, device fabrication details and characterization, DSC plots, TGA plots, cyclic voltammetry, and AFM measurements.

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