Molecular design for all-in-one self-assembled donor–acceptor organic solar cells

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A R T I C L E I N F O

Keywords:
All-in-one donor acceptor molecule
Amphiphilic bilayer sheets
Organic solar cells
Self-assembly
Molecular dynamics simulations

A B S T R A C T

The stability of organic solar cells still remains one of the main challenges to make this technology suitable for large scale mass production. The stability of the morphology is one main degradation channel in currently used bulk heterojunction systems. We introduce three different all-in-one donor–acceptor amphiphilic triads and perform molecular dynamics simulations in order to investigate the stacking of the donor and acceptor sub-molecules after performing a simulated annealing step. We show that the molecular volume of each sub-molecule of the triad plays an important role for the stability of the z-stacking within the bilayer sheet. Further, we found that TIPS-pentacene and TIPS-tetraazapentacene sub-molecules serving as donor and acceptor, respectively, keep their crystalline nature in the bilayer sheet. Thus, by such a system, charge carrier mobilities in the range of 1 cm²/Vs should be possible, which is three orders of magnitude higher compared to measured mobilities in existing highly efficient organic solar cells. Therefore, by this approach not only the stability can be increased, but also the fill factor and therefore the power conversion efficiency can be improved.

1. Introduction

With the usage of non-fullerene-acceptors, in the last years the power conversion efficiency of organic solar cells has been increased to 18% [1–3]. However, degradation still prevents this technology in commercial applications. It has been shown that photo-oxidation of the acceptor material and the instability of the bulk heterojunction morphology and its interface are one of the main degradation mechanisms of these highly efficient organic solar cells [4–6]. In order to overcome these issues it has been proposed to design photochemically more stable absorber materials or/and to increase the glass transition temperature of the polymer by side-chain and backbone engineering, lowering the diffusivity of acceptor molecules into the donor polymers [4–6]. The voltage losses in organic solar cells are higher compared to their inorganic counterparts. Burke et al. proposed to lower the voltage losses by about 0.4 V by a number of optimizations: (1) reducing the volume fraction of the mixed phase from 50% to 1%, 2) Increasing the charge transfer (CT) lifetime from 100 ps to 10 ns. 3) Decreasing the interfacial disorder from 100 to 50 meV 4) Lowering the CT binding energy from 200 meV to 50 meV and 5) Decreasing the number of CT states per interface from 30 to 3 [7]. Panhans et al. proposed to lower the non-radiative recombination and therefore the voltage losses by rigidification of the absorbing molecules, orbital delocalization, increasing the number of molecular neighbors, and by similar molecular orbital shapes of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) [8]. Similarly, Azzouzi et al. showed that lowering the reorganization energy of the absorbing molecules would increase the voltage by about 0.2 eV [9]. Therefore, a high stiffness and tightly packed material might be beneficial to increase the voltage and would also lower the diffusivity of the acceptor molecule into the donor polymer and therefore improve the long term stability. These molecular wishes point to the need for a more crystalline material. However, the low exciton diffusion length of 5–22 nm in the absorber material needs an interpenetration of the donor and the acceptor phase in this range [10], preventing the usage of more crystalline materials. This dilemma and the issues mentioned above can, in principle, be solved by covalently bonded and well ordered donor–acceptor molecules. An order between donor and acceptor moieties of such a system can be achieved by amphiphilic side chains. It has been shown that amphiphilic dyads can generate free charges after photoexcitation [11]. However, in order to suppress the recombination of free charges it is proposed to include a spacer molecule in between the donor and the acceptor [12], lowering the exciton binding energy into the range of the thermal energy (~ 25 meV) [13]. It has been experimentally shown that covalently bonded donor–spacer–acceptor molecules, or triads, are able to separate charges by a step-wise charge transfer process [14,15], exhibiting lifetimes in the order of nanoseconds [14,16], and can exhibit...
photovoltaic properties [17,18]. The power conversion efficiencies of a photovoltaic device consisting of triads are, if reported, negligible (up to 0.035% [17,19,20]). Reports about molecules consisting of a donor, spacer, and an acceptor moiety can fail in charge separation if their \(\pi\)-system is not interrupted, leading to an unseparated lowest CT state with a high Coulomb binding energy (\(\approx 0.5\) eV [21]) and therefore large geminate recombination losses. For triads with an interrupted \(\pi\)-system between the three moieties, the dissociation of the exciton is successful [14,15] and the recombination time is increased [22]. However, in this case the reason for low efficiencies can mainly be attributed to an inefficient charge transport of electrons and holes to their respective electrodes. Therefore, triads exhibiting the needed physical properties for efficient and stable photovoltaic devices have not been implemented so far, even though outstanding photovoltaic properties are expected.

Amphiphilic triads, in principle, can agglomerate into bilayer sheets. As shown in Fig. 1, by orienting the bilayer sheet perpendicular to the substrate, i.e. the molecular axe is in parallel to the substrate, an ideal morphology for organic solar cells is obtained. The charge generation of the donor–acceptor system is similar as in conventional bulk heterojunction devices, but exhibits one more interface. An energy step between the donor and also between the acceptor sub-molecules is. Therefore, we use molecular dynamics simulations (MD) to obtain information how the molecules involved do behave mechanically in a simulated annealing step. Based on these investigation, we give an answer how photovoltaic triads can be designed to obtain a stable morphology.

2. Computational details

MD simulations are performed to obtain the stability of the bilayer sheets, consisting of amphiphilic triads. The idea is to perform a simulated annealing by MD simulations on the pre-equilibrated bilayer sheet, giving an insight into the stability of the \(\pi\)-stacking and of each molecule in the bilayer formation.

All quantum mechanical (QM) calculations, carried out exploiting the density functional theory (DFT) were performed with the Gaussian16 suite of programs [28]. All QM calculations on single molecules were performed using the range separated hybrid functional CAM-B3LYP with the 6-31G+(d,p) polarized basis set. All classical molecular mechanics (MM) optimizations and MD simulations were performed by the Gromacs2019.4 software [29].

For MD simulations, the parametrization of the Forced Fields (FF) of the amphiphilic triad is divided into its sub-parts, i.e. the apolar side-chain, the acceptor, the spacer, the donor, and the polar side-chain. The FF of the alkyl and the oligo(ethylene glycol) side-chains have been derived from the General Amber Force Field (GAFF).

The parametrization of the three sub-molecules of the triad has been performed separately for the intra- and intermolecular terms using JOYCE and PICKY software, respectively [30–32]. These tools allow the parametrization of organic molecules based on DFT calculations. The molecular structures of the triads studied are shown in Fig. 2. For each unit of the triad, the intramolecular parameters were determined using JOYCE software based on geometries, energies and Hessian ground state matrices, intentionally calculated at the QM level. The JOYCE standard protocol was followed, minimizing the least square difference between MM and stored QM data. For the intermolecular part, the FF parameters that determine the interaction between different molecules (i.e. Lennard-Jones and point charges) were determined using PICKY software. The standard PICKY procedure was used, which is based on a nonlinear least squares fit between the interaction potential energy surface (IPES) calculated at the QM level and the surface obtained at the MM level with the PICKY FF. To reliably sample the IPES, the interaction energies of several (> 200) dimers were calculated. At the QM level the empirical Grimme correction (GD3 [33]) was used to account for dispersion. To deal with the basis set superposition error (BSSE), the standard counterpoise correction was applied in all cases [34]. As before for the intramolecular term, parametrization was performed separately for each moiety (donor, spacer, and acceptor).

Finally, the parametrization of the entire amphiphilic triad is achieved by combining the intra- and inter-molecular parameters into one parameter set by a self-written python script. For more details on the parametrization we refer to Ref. [13].

Using the intra- and inter-molecular parameters, MD simulations can be performed. We first used a self-written python script to put the amphiphilic triads into a bilayer sheet-like starting position, representing an unequilibrated box filled with about 1000 amphiphilic triads. The simulation box with periodic boundary conditions is then
used to perform an energy minimization step, a isothermal (NVT), and a isobaric ensemble (NPT) calculation. The pre-equilibrated system is then used as starting geometry for the simulated annealing calculations, with temperatures increasing from 300 K to 395 K and then back to 300 K, whereas the 395 K are kept for 5 ns. We used a Berendsen thermostat with coupling constant 0.1 ps, a Parrinello–Rahman barostat with a time constant of 8 ps, the reference pressure was set to 1 bar, whereas the time step was set to 1 fs.

In order to quantify the error between the FF obtained and DFT simulations, for intramolecular forces we compared the normal modes with its frequencies as well as the energy-function dependent on dihedral angles. As shown in supporting information in Fig. 1, the frequencies obtained for each normal mode excellently fit to the DFT results. Furthermore, also the energy of the angle dependent dihedrals in the different molecules energetically fit very well to the QM computed configurations (supporting information Figure 2–6). The parametrization of the bulky TIPS side chains is more complicated, since three dihedrals interfere with each other. This problem has been solved by computing each possible configuration between the 3 dihedrals with an angle accuracy of $30^\circ$ (supporting information Figure 7 and 8). Due to the complexity of the QM interaction of the three dihedrals, the absolute energy values could not be fitted accurately. However, the overall trend could be resolved very well. For the intermolecular forces, the interaction of several hundreds of dimers are fitted until an addition of 50 new dimers delivers a standard deviation which is less than 1 kJ/mol. This satisfies the convergence criteria and gives the maximum accuracy based on the given set of parameters.

We aim to find a triad with a crystalline and temperature stable $\pi$-stacking of donor sub-molecules on each other and acceptor sub-molecules on each other. In order to quantify the MD-simulation we extract by a self-written python script the mean $\pi$-stacking distance and the $\pi$-system overlap from each molecule to its four closest neighbors, as depicted in Fig. 3. In this script the $\pi$-system overlap is defined by the area overlap of the projection of the $\pi$-system of the four neighboring molecule onto the $\pi$-system of the molecule of interest, whereas the $\pi$-system area is simply defined by the area spanned by the atoms involved in the $\pi$-system plus the hydrogen atoms attached to the $\pi$-system. For a molecule with a overlap of 100% the $\pi$-system area on both molecule sides would fully be covered by the four adjacent molecules. The $\pi$-stacking distance reflects the difference from the atomic $\pi$-system middle points projected to the $\pi$-system normal of the molecule of interest. According to Ref. [35], increasing the $\pi$-stacking distance of a pentacene dimer from 3.5 Å to 5 Å, reduces to electronic coupling from 411 to 41 meV, which is a factor of 10, leading to a hopping probability and thus to the charge carrier mobility which is decreased by a factor of 100 [35,36]. Thus, the $\pi$-stacking distance is crucial for high charge carrier mobility materials, but also makes the system more stiff, lowers the reorganization energies, and improves the stability and the voltage losses.

3. Results

3.1. Density and temperature vs. annealing time

The temperature and density over time of each material is shown in Fig. 4. The simulated annealing step starts at room temperature (300 K), increases to 395 K for 5 ns and then cools down again to room
temperature. The density of CyanoPDI-BDOPV-TDI and CyanoPDI-PDI-TDI initially increases but saturates after three to four nanoseconds. The APen-TTDA5T-Pen triad seems to be already fully equilibrated at the beginning of the simulation, since in this triad the density only depends on the temperature and not on the time. Therefore, in all three simulations the final geometry at room temperature is an equilibrated structure.

In the following results we only investigate this final equilibrated structure of the bilayer sheets based on the three amphiphilic triads.

### 3.2. Final \( \pi \)-stacking and overlap values in comparison

First, we want to emphasize that each material could conserve its bilayer structure through the annealing step. However, their \( \pi \)-stacking properties strongly differ from each other. Table 1 shows the average values obtained. The triad APen-TTDA5T-Pen exhibits an overlap of 53% and 57% for the acceptor (tetraazapentacene) and donor (pentacene) molecule, respectively. By simulating pure TIPS-Pentacene in its crystalline structure an overlap of 58% is obtained. Thus, the crystalline structure of pentacene and tetraazapentacene is not significantly affected by the molecular triad and the bilayer sheet. The \( \pi \)-stacking distance of pentacene and tetraazapentacene is 3.39 Å and 3.36 Å, respectively. These values are close to the reported values for the \( \pi \)-stacking of 3.28 Å for tetra-azapentacene [37] and 3.3 Å for TIPS-Pentacene [38], supporting the reliability of the parameterization procedure with JOYCE and PICKY. In the triads CyanoPDI-PDI-TDI and CyanoPDI-BDOPV-TDI the \( \pi \)-stacking distance of the donor TDI is 3.27 to 3.29 Å, respectively, reflecting the extended \( \pi \)-system with its increased attraction. The CyanoPDI sub-molecule exhibits the largest \( \pi \)-stacking distance of 3.68 to 3.69 Å. However, both triads based on TDI and CyanoPDI do have a lower \( \pi \)-system overlap area in the range of 41% to 44%.

### 3.3. Cross-section area of sub-molecules involved

Since the used conjugated sub-molecules are stiff, their molecular volume with respect to its length, i.e. the cross-section area, is crucial for self-assembly and specially for the orientation of the sub-molecules to each other. As shown in Table 2, we calculated the cross-section area by dividing the molecular volume of each sub-molecule with its length along the backbone (without linker molecules). The molecular volume was calculated according to Ref. [39] with a radius of 0.5 Å in the high resolution mode.

The cross-section areas of the spacer TTDA5T compared to the pentacene based sub-molecules are quite different, while CyanoPDI-PDI-TDI and CyanoPDI-BDOPV-TDI exhibits sub-molecules with similar cross-section areas.

### 3.4. Packing of APen-TTDA5T-Pen

Fig. 5 shows a map of the structure of the acceptor and donor phase represented by a dot with a color corresponding to the average \( \pi \)-stacking distance to its four neighbors, whereas the position of the dot represents the center of the respective sub-molecule. Within the scale used for the \( \pi \)-stacking distance, no significant distribution can be found, supporting the fact that tetraazapentacene and the pentacene sub-molecule are in a crystalline structure in their molecular phase. The molecular shape of four representative amphiphilic triads are shown in Fig. 6. We see that the pentacene and tetraazapentacene backbones are shifted but on top of each other, supporting the high overlap value obtained which means that this donor and acceptor sub-molecule exhibit the same crystalline structure in the bilayer sheet, as in its single crystal structure, which is a brick wall structure. As in their crystal structure, the pentacene and tetraazapentacene backbones are slightly tilted with respect to the stacking direction due to the present bulky TIPS derivative. The triad in the simulated bilayer sheet is not linear but shows a zig-zag shape. In order to understand this, the cross-section area of the sub-molecules must be considered. Initially, as shown in Fig. 2, the APen-TTDA5T-Pen triad is positioned linearly (no zig-zag shape). The cross-section area, see Table 2, of the pentacene based molecules is around 73 Å\(^2\), while the TTDA5T exhibits a cross-section area of 43.9 Å\(^2\). Therefore, initially the local density in the pentacene and tetraazapentacene area is much higher as compared to the TTDA5T sub-molecule area. During MD simulations the TTDA5T sub-molecules attract each other, leading to an increased local density. This attraction and the subsequent increase in its local density, however, can only take place if an angle between the backbones of TTDA5T and pentacene (or tetraazapentacene) establishes. By this mechanism the initially different local densities equilibrate, which lowers the overall energy of the system.

### Table 1
Mean \( \pi \)-stacking distance (Å) and in brackets mean molecular overlap (%).

<table>
<thead>
<tr>
<th>Triad (acceptor–spacer–donor)</th>
<th>Acceptor</th>
<th>Donor</th>
</tr>
</thead>
<tbody>
<tr>
<td>APen-TTDA5T-Pen</td>
<td>3.36 Å (53%)</td>
<td>3.39 Å (57%)</td>
</tr>
<tr>
<td>CyanoPDI-PDI-TDI</td>
<td>3.68 Å (42%)</td>
<td>3.27 Å (44%)</td>
</tr>
<tr>
<td>CyanoPDI-BDOPV-TDI</td>
<td>3.69 Å (41%)</td>
<td>3.29 Å (43%)</td>
</tr>
</tbody>
</table>

### Table 2
Geometrical properties of sub-molecules.

<table>
<thead>
<tr>
<th>Name</th>
<th>Volume</th>
<th>Length</th>
<th>Cross-section area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pen</td>
<td>1087 Å(^3)</td>
<td>14.8 Å</td>
<td>73.4 Å(^2)</td>
</tr>
<tr>
<td>CyanoPDI</td>
<td>551 Å(^3)</td>
<td>11.4 Å</td>
<td>48.5 Å(^2)</td>
</tr>
<tr>
<td>PDI</td>
<td>498 Å(^3)</td>
<td>11.5 Å</td>
<td>43.4 Å(^2)</td>
</tr>
<tr>
<td>TDI</td>
<td>657 Å(^3)</td>
<td>15.7 Å</td>
<td>42.0 Å(^2)</td>
</tr>
</tbody>
</table>

### Fig. 5
Structural map of molecular center of tetraazapentacene and pentacene sub-molecules after the simulated annealing step. The color of each dot refers to the mean \( \pi \)-stacking distance of the respective sub-molecule to its four closest neighbors (the scale is adjusted and kept for the following map plots).

### Fig. 6
Four representative amphiphilic triads (APen-TTDA5T-Pen) present in the bilayer sheet after the simulated annealing step. The polar side-chains are in the middle, followed symmetrically by the sub-molecules tetraazapentacene, BDOPV, pentacene, and the alkyl side-chains.
The geometrical distribution of the center similar as the cross-section area of the CyanoPDI sub-molecule, see cross-section area of the BDOPV is higher compared to the TDI, but molecular shape with respect to the rylene based sub-molecule. The diffusion between the different phases (donor, spacer, and acceptor). One root to overcome this interdiffusion might be using a spacer sub-molecule from the triad CyanoPDI-PDI-TDI is shown. Compared to the APen-TTDA5T-Pen bilayer sheet, the position of the donor and acceptor molecule exhibits a much broader distribution with respect to the \(x\)-axis, also reflected by the lower overlap value of 42\% and 44\%, summarized in Table 1. This distribution along the \(x\)-axis and also the distribution of \(\pi\)-stacking distance, which is much larger, clearly shows that no crystalline donor or acceptor phase are present in this bilayer sheet. In Fig. 8 it is shown on the left hand side that the perylene backbones can stack very closely on each other, whereas on the right hand side one of the two triads exhibits a zig-zag shape. The cross-section areas of the TDI and PDI are similar, 42 Å\(^2\) and 43.4 Å\(^2\), respectively, while the CyanoPDI is a bit larger (48.5 Å\(^2\)). This difference in density might not be enough, as compared to the APen-TTDA5T-Pen triad, to induce an angle between the submolecules, destabilizing the donor and acceptor phase. Further, the rylene based sub-molecules exhibit disk like shapes, making a slipping of sub-molecules into their neighboring phases more likely. In this triad the only correcting force against the interdiffusion of the sub-molecule are the amphiphile side-chains, keeping the overall bilayer sheet stable but cannot avoid a local diffusion between the different phases (donor, spacer, and acceptor). One root to overcome this interdiffusion might be using a spacer molecule with a different molecular shape as compared to the donor and the acceptor sub-molecule, which will be investigated in next section.

3.6. Packing of CyanoPDI-BDOPV-TDI

In this triad the BDOPV with its side-chains exhibit a different molecular shape with respect to the rylene based sub-molecule. The cross-section area of the BDOPV is higher compared to the TDI, but similar as the cross-section area of the CyanoPDI sub-molecule, see Table 2 for comparison. The geometrical distribution of the center points in Fig. 9 with respect to the \(x\)-axis is smaller as compared to distribution from the CyanoPDI-PDI-TDI triad shown in Fig. 7. This effect is more pronounced in the TDI sub-molecule. The interdiffusion within the donor, spacer, and acceptor phase has been suppressed by the different spacer molecule. We assume that the side-chains of the BDOPV, pointing out of the molecular plane, hinder its diffusion into the disk like donor and acceptor phases. In Fig. 10 it can be recognized that the side-chains of the neighboring BDOPVs are entangled with each other. These intermolecular entanglement certainly also increases the intermolecular forces in the BDOPV phase, which might be an additional reason for the suppressed interdiffusion of the BDOPV spacer sub-molecules.

4. Discussion

Based on the higher order obtained in CyanoPDI-BDOPV-TDI compared to CyanoPDI-PDI-TDI one would expect a larger overlap, which is surprisingly not the case, i.e. the overlap of the CyanoPDI-PDI-TDI and CyanoPDI-BDOPV-TDI is almost the same (see Table 1). This can be explained by a similar local order between neighboring donor or acceptor sub-molecules, while the distribution within about thousand simulated molecules still can be larger. This assumption is also supported by the very similar mean \(\pi\)-stacking distance of the CyanoPDI-PDI-TDI and the CyanoPDI-BDOPV-TDI triad.

The pentacene based triad APen-TTDA5T-Pen exhibits the lowest density of 0.95 g/cm\(^3\) but the highest order in the donor and acceptor phase. Similarly, CyanoPDI-BDOPV-TDI shows a higher order but a lower density, compared to CyanoPDI-PDI-TDI. Thus interestingly the lower the density the higher the order in the donor and acceptor phase. The reason for that is not clear. It might be such that for an optimal \(\pi\)-stacking in the donor and acceptor phase as less as possible interaction with the spacer is beneficial. Thus, to increase the order in the donor and acceptor phase of the perylene based triads a decoupling
between the donor and spacer as well as between the spacer and the acceptor could be advantageous. This can be achieved e.g. by a larger unconjugated linker molecule. However, a larger linker molecule also increases the distance between the donor, the spacer, and the acceptor phase, leading to a lower charge transfer probability (Marcus theory [36]), which is needed for an efficient working solar cell.

The \( \pi \)-stacking distance and its overlap in CyanoPDI-PDI-TDI and CyanoPDI-BDOPV-TDI are very similar. For an efficient functioning solar cell the direct interface between the donor and acceptor material must be minimized, lowering the recombination of photogenerated charges. Thus, from this perspective the CyanoPDI-BDOPV-TDI triad is the more promising candidate for an all-in-one organic solar cell. Further, BDOPV absorbs in a larger spectral range which is also important for a efficient solar cell [27,40].

As mentioned, the order of the donor and acceptor phase of APen-TTDA5T-Pen triads in a bilayer sheet is very similar to their respective crystal structure. Based on that the charge carrier mobility in the donor and acceptor phase should be in the range of 1 cm\(^2\)/Vs, which is three orders of magnitude higher compared to currently most efficient organic solar cells [1,24]. Due to the reduced disorder and interface area the charge carrier recombination in this system is maximally reduced, which presumably would lead to record fill factors in organic solar cells.

However, some questions remain. Are these bilayer sheets also formed spontaneously in solution or by a heat treatment? Such a investigation would need a simulation time which is currently beyond our capabilities without doing further approximations, by e.g. coarse grain techniques.

Due to the linear shape of CyanoPDI-PDI-TDI and CyanoPDI-BDOPV-TDI and its mentioned distribution along the \( \pi \)-axis, we expect that those two bilayer sheet would form in solution or by an annealing step. However, we are not sure about this point in the case of APen-TTDA5T-Pen. The TIPS side-chains of pentacene and tetraazapentacene backbones are responsible for the stable stacking behavior during the simulated annealing step, since the bulky TIPS hinders the pentacene and tetraazapentacene to shift out of the \( \pi \)-stack, they might also hinder them by steric hindrance to establish the brick wall structured \( \pi \)-stack during self-assembly. This of course strongly depends on the experimental parameters. It might also be possible to support the self-assembly by directive high electric fields. Another question would be, how tolerant such a system is to defects. E.g. what happens if a triad is accidentally placed in the opposite direction, building up recombination centers in the donor and acceptor phase? These questions need to be answered by further investigations theoretically or by experiments.

5. Conclusion

We have introduce three different amphiphilic all-in-one donor–acceptor triads for presumably highly efficient and stable organic solar cells. We conducted simulated annealing by molecular dynamics simulation at about 120 °C for 5 ns.

By MD-simulations we could show that by using similar cross-section areas for the donor, spacer, and acceptor sub-molecules the donor or acceptor sub-molecules do shift out of their phase, which presumably lowers the charge carrier mobility. In order to prevent that we investigated a spacer sub-molecule with a different shape (BDOPV), i.e. with side-chains, which interact strongly with neighboring side-chains, stabilizing the extend of shifting donor or acceptor molecules out of their phase. However, a different spacer does not significantly change the calculated mean overlap of between \( \pi \)-systems, nor it did influence the mean \( \pi \)-stack distance.

In order to make the \( \pi \)-stack more stable we conclude that the molecular volumes, or more accurately, the cross-section areas of the sub-molecules should be different. This induces an angle in the triad, a zig-zag shape, preventing a shift of the respective sub-molecule out of its phase.

The triad based on pentacene and tetraazapentacene (APen-TTDA5T-Pen) provide a perfect crystalline morphology in the two dimensional sheet of the donor and of the acceptor phase, comparable with their single crystalline material, which exhibits charge carrier mobilities around 1 cm\(^2\)/Vs [24]. The reason for the crystalline and stable donor and acceptor phase is the zig-zag shape of the triad and therefore the different present cross-section areas in the sub-molecules involved. Additionally, the bulky TIPS side chain of the pentacene and tetraazapentacene, prevents the molecule to escape from the “brickwall” \( \pi \)-stack.

Based on these findings it is clear that the most promising candidate for synthesis would be the amphiphilic triad APen-TTDA5T-Pen. Thus, we strongly want to motivate chemists to synthesize the reported amphiphilic triads or similar molecules.

6. Design rules and future challenges

For a successful \( \pi \)-stacking and stable bilayer sheet we propose to choose a cross-section area of the spacer sub-molecule which should be significantly different to at least one of its neighbors. We also recommend to use a linear spacer molecule with alkyl side-chains to increase not only the solubility, but also to enforce the entanglement in the spacer phase, which does not need to be crystalline. Further we propose to use disk-like donor and acceptor molecules, which lowers the \( \pi \)-stacking distance and therefore increases the charge carrier mobilities.

There are two main challenges for all-in-one molecular solar cells. One challenge is to find an amphiphilic triad which does not only build stable \( \pi \)-stacks but also can be synthesized with a certain yield.

The second challenge is to contact the donor or acceptor phase electrically. If amphiphilic molecules are applied on an oxide substrates (which is polar) the polar end of the molecules will point to it, and vice versa for apolar treated substrate the alkyl chain will most probably point to the substrate. Both conformations do not provide the device architecture as shown in Fig. 1, since the conducting pathways along the donor or the acceptor phase are in parallel to the substrate, leading to high contact resistances for both, the electron and hole extraction. In order to overcome this problem the conducting pathways could be forced to lie in perpendicular to the substrate by external fields, or the substrate surface energy might be tuned (and maybe nano-structured) by self-assembled-monolayers.

CRediT authorship contribution statement

Stefan Kraner: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. Lukas Schmidt-Mende: Supervision, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

We are thankful for the discussions with Marvin Unruh, Dr. Sybille Allard, Prof. Dr. Ulrich Scherf from the Bergische Universität Wuppertal. We also want to thank Giacomo Prampolini for his ongoing support for issues with molecular dynamics simulations and specially for its parametrization. The authors acknowledge support by the local HPC resources through the core facility SCCKN. The authors further acknowledge support by the state of Baden-Württemberg through bwHPC and the German Research Foundation (DFG) through grant no INST 40/575-1 FUGG (JUSTUS 2 cluster). This work has been financially supported by DFG Project Nr. 419282603, KR 5044/3-1.
