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# Revisiting the Optimal Nano-Morphology: Towards Amorphous Organic Photovoltaics

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**Abstract:** Organic photovoltaic cells commonly use an active layer with a polycrystalline bulk heterojunction. However, for simplifying the fabrication process, it may be worthwhile to use an amorphous active layer to lessen the burden on processing to achieve optimal performance. While polymers can adopt amorphous phases, molecular glasses, small molecules that can readily form glassy phases and do not crystallize over time, offer an appealing alternative, being monodisperse species. Our group has developed a series of reactive molecular glasses that can be covalently bonded to chromophores to form glass-forming adducts, and this strategy has been used to synthesize glass-forming donor and acceptor materials. Herein, the results of devices incorporating these materials in either partially or fully amorphous active layers are summarized. Additionally, these molecular glasses can be used as ternary components in crystalline systems to enhance efficiency without perturbing the morphology.

Keywords: organic photovoltaics, bulk heterojunction, amorphous, molecular glasses, triazines

## 1. Introduction

The crystallization behavior of organic compounds, in particular small molecules, is abundantly studied.<sup>[1,2]</sup> While predicting and controlling the crystal nucleation and growth processes, and crystalline packing, may still be the object of exhaustive studies, like physical-organic research, the fact that organic small molecules tend to spontaneously crystallize is widely accepted.<sup>[1,2]</sup> However, a lesser-known fact is that several organic small molecules can also form glassy phases, which are amorphous, when cooled from the melt.<sup>[3-7]</sup> To achieve this, the compound must reach a temperature where molecular diffusion becomes too slow for the molecules to reach positional and directional order. Instead, the molecules reach a state where they are randomly oriented, like in a liquid, but where movement is halted. The temperature at which this occurs is called the glass transition temperature  $(T_a)$ .<sup>[8,9]</sup> In most cases, very fast cooling rates are necessary to reach the glassy state. Moreover, as glasses are thermodynamically metastable, most small molecules in the glassy state tend to crystallize when heated past their Tg, or even over time on standing at ambient temperature. Nonetheless, there exist small molecules that can readily form stable glasses, even upon slow cooling, that remain indefinitely in the glassy state under ambient conditions. These compounds are called molecular glasses, or amorphous molecular materials.<sup>[10-14]</sup>

While most polymers are known to form glasses, and consequently are often used in applications involving optical

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quality thin films, small molecules offer the advantages of being easier to purify, characterize and process. Moreover, as small molecules are monodisperse species, they lead to higher batch homogeneity, provided that the compounds can be designed to properly resist crystallization. Fortunately, with recent research efforts, guidelines have emerged that allow to predict with some degree of accuracy whether a particular molecular structure will readily form long-lived glasses. For example, compounds with irregular and non-planar structures, with low symmetry, that can adopt several conformers of similar energy with high interconversion barriers, or that can participate in a number of redundant intermolecular interactions, tend to show a higher propensity to form glasses because of slower crystallization kinetics. As a result, the fields of application for molecular glasses are diversified, and include pharmaceutical formulations,<sup>[15–17]</sup> nanolithography,<sup>[18,19]</sup> photonics<sup>[20,21]</sup> and opto-electronics, in particular OLEDs.<sup>[13]</sup> In principle, molecular glasses could potentially be used in any application involving organic thin films or polymers, including but not limited to, photovoltaics.

Owing to the tremendous success of the so-called bulk heterojunction (BHJ),<sup>[22]</sup> most organic photovoltaic materials developed to date have been based on polymer materials. The success of the BHJ architecture holds on the entropic nature of the phase separation: the so-called spinodal decomposition, which is a fate of linear polymer chains.<sup>[23,24]</sup> However, spinodal decomposition is also a burden of polymer blends, which most often evolve spontaneously until total separation under temperature or stress, unless crosslinked by any means. Small molecules, on the other hand, also tend to crystallize over time. However, with careful molecular design, it is possible to generate molecular glasses that remain in the amorphous state for extended periods of time, even at temperatures above  $T_{e^*}^{[3-7]}$  Another burden with polymers is the present situation of recycling,<sup>[25]</sup> which is not sufficiently developed to avoid their dispersion all over the oceans. The present status is that some countries aim at banning nonrecyclable polymers. In such situation, it is becoming

increasingly difficult to bring new polymer structures to large-scale commercial applications.

To attempt the replacement of polymers in organic photovoltaics, researchers have developed crystalline smallmolecule organic materials. The processing techniques used for these materials are mostly based on vacuum deposition. which is costly and difficultly applicable to large surfaces and flexible substrates. On the other hand, high-performance crystalline small-molecule photovoltaic materials that are processable from solution often require stringent processing conditions, like specific solvents, deposition temperature, and critical post-deposition processing conditions.<sup>[26-31]</sup> In spite of this, it is nonetheless crucial to optimize the fabrication process with crystalline materials to reach optimal device performance, as a recent study uncovered that there was a stronger correlation between device performance and device morphology (which is directly correlated with the fabrication process) than with the energy level tuning of the individual components.<sup>[32]</sup>

The question of amorphous vs. crystalline materials for organic OPV mirrors that of the material used in the first generation of commercial PV panels: silicon. Although singlecrystal silicon, which is used for integrated circuits, is known to yield higher conversion efficiencies, polycrystalline Si offers an alternative where efficiency is slightly lower but manufacturing is simplified with a faster production rate. On the other hand, amorphous Si allows to fabricate devices more easily and more predictably, and the milder deposition conditions allow them to be deposited on various substrates (e.g. plastic) and used in niche applications (e.g. small portable solar-powered devices).<sup>[33]</sup> However, the slower progress curve of amorphous vs. crystalline semiconductors is related to the status of amorphous semiconductor physics, which is still in development for specific materials like small molecules.<sup>[34]</sup>

Unlike Si, organic materials used in bulk heterojunction organic photovoltaics are difficult to crystallize in large enough single crystals to be cut into wafers and used in commercial panels. Furthermore, a blend of two materials (donor and acceptor) is used, and the optimal morphology is a polycrystalline thin film composed of a random patchwork of percolated nanocrystalline donor and acceptor domains. The optimal domain sizes were found to be around 10-20 nm to allow the excitons to diffuse and dissociate before recombination.<sup>[35]</sup> This contrasts with Si, where there are no excitons, and where polycrystalline domains are on the order of >1 mm, with few grain boundaries which lead to lower efficiencies.<sup>[36]</sup> In comparison, the bulk heterojunction architectures of organic PV cells show very small (10-20 nm) crystalline domains, with a significantly higher density of grain boundaries, acting as charge traps.<sup>[37-39]</sup> As a result, the long-range order present in the active layers of polycrystalline OPV devices is actually closer to that of amorphous Si than to that of polycrystalline Si. The difference between amorphous and polycrystalline BHJ is therefore expected to be less pronounced than that between amorphous and crystalline Si. Moreover, as was discussed previously, if the morphology of polycrystalline OPV devices has a more pronounced impact on their performance than the selection of donor and acceptor materials,<sup>[32]</sup> using amorphous donors and acceptors is likely to deemphasize the impact of morphology because the molecules will then be guaranteed to be oriented in a random fashion and yield a continuous and isotropic active layer, which would lead to a higher predictability of device performance by the selection of the active layer materials by energy level tuning.

Other groups have also successfully fabricated OPV cells using molecular glasses (1–3, Scheme 1),<sup>[40–42]</sup> and PCE up to 3.5% were obtained with triazatruxene derivative **2b** as donor and PC<sub>71</sub>BM as acceptor. The photovoltaic parameters of the best-performing devices for each material are listed



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Scheme 1. Molecular structures of compounds 1-3.

below in Table 1. This demonstrates that at least partially amorphous active layers (the PCBM fraction may still crystallize) are viable to reach decent efficiencies in OPV cells. However, these studies do not provide accurate comparisons between crystalline and amorphous materials: either the amorphous materials were not compared with closely related crystalline analogues,<sup>[40,41]</sup> or the comparisons were not accurate because the chromophore was significantly altered, making it impossible to determine the origin of the difference in efficiency.<sup>[42]</sup>

While studying glass formation in mexylaminotriazine derivatives,<sup>[43,44]</sup> the fact that one of the arylamino groups could be substituted for various aryl- or alkylamino substituents while retaining glass-forming ability gave rise to the idea of a modular strategy to use these glass-forming compounds to induce glass formation in various chromophores through a simple covalent bond linkage.<sup>[21,45]</sup> Indeed, molecular glasses containing various reactive functional

groups, including thiol **4**, amines **5–6**, and rhodanine 7, could be readily designed and synthesized, then reacted with dyes (Scheme 2).<sup>[46–48]</sup>



Scheme 2. Molecular structures of compounds 4–7, and general scheme of functionalization reactions.

While there are other moieties known to be capable to induce glass formation in chromophores, including triarylamines (8),<sup>[20,49]</sup> triphenylmethanes (9)<sup>[50]</sup> or diphenylhydrazones (10)<sup>[51]</sup> (representative compounds are shown in Scheme 3), the main appeal of this method is that the mexylaminotriazine groups can be readily introduced at the last step of the synthesis and allow a divergent approach where few molecular glasses with complementary reactive groups can be used to functionalize a wide range of electron donors and acceptors, and the adducts reliably share the glassforming properties of their precursors, thereby eliminating the need of screening glass-forming structures through trial and error. Furthermore, the functionalizable triazine glasses can be synthesized in high yields from typically cheap precursors.

<sup>&</sup>lt;sup>1</sup>Marvin was used for drawing, displaying and characterizing chemical structures, substructures and reactions, Marvin 17.4.3, 2017, ChemAxon (www.chemaxon.com).

Donor	Acceptor	D:A Ratio	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	PCE (%)	Ref.
Molecular G	lass Donor						
1a	PC <sub>71</sub> BM	1:4	093	5.50	34.4	1.76	38
1b	$PC_{71}BM$	1:3	0.89	7.86	35.3	2.47	38
2a	$PC_{71}BM$	$1:5^{[a]}$	0.80	8.1	45	2.9	39
2b	$PC_{71}BM$	$1:5^{[a]}$	0.83	9.4	45	3.5	39
3	$PC_{71}BM$	1:2	0.81	6.28	37	1.86	40
15	$PC_{61}BM$ <sup>[b]</sup>	1:1	0.42	3.20	45	0.44	46
15	$PC_{61}BM$ <sup>[c]</sup>	1:1	0.49	2.96	39	0.52	46
Molecular G	lass Acceptor						
P3HT	11b	1:2	0.62	2.48	43.0	0.66	44
P3HT	12b	1:2	0.64	2.33	42.6	0.63	44
P3HT	13	$1:2^{[d]}$	0.83	4.58	67	2.50	45
P3HT	14	$1:2^{[d]}$	0.84	3.60	53	1.56	45
Molecular Glass Donor/Acceptor							
15	13	1:1	0.42	2.55	42	0.41	46
Molecular G	lass Ternary Acceptor						
P3HT	PC <sub>61</sub> BM	1:1	0.58	8.70	54	2.80	68
P3HT	PC <sub>61</sub> BM/ <b>12b</b>	1:1:0.2	0.66	11.13	53	3.86	68
P3HT	PC <sub>61</sub> BM/ <b>13</b>	1:1:0.15	0.62	11.85	62	3.80	68
[a] 0.6% 1.8-diiodooctane was used as additive. [b] Homogeneous blend. [c] Phase-segregated blend. [d] Conventional device.							

Table 1. Photovoltaic parameters of devices fabricated with molecular glasses as active layer materials.



Scheme 3. Molecular structures of compounds 8-10.

In the context of small-molecule donors and acceptors for OPV, various functionalizable groups are present in most chromophores. For example, in perylenediimides (PDI), it is possible to introduce functionality at the imide positions,<sup>[52]</sup> or alternatively, the bay positions can be brominated then substituted with various nucleophiles.<sup>[53–55]</sup> In most electron donor materials, electron-withdrawing groups are typically located peripherally, typically dicyanovinyl, cyanoacetyl, or alkylrhodanine groups, which are all synthesized from the respective aldehydes by Knoevenagel condensations.<sup>[56–57]</sup> While the dicyanovinyl group does not allow for further substitution, rhodanines, cyanoacetates or cyanoacetamides can be introduced onto molecular glasses.

The present situation with amorphous small-molecule photovoltaics is reminiscent of the situation of organic photovoltaics before 2000, when researchers were working arduously at achieving record PCEs in the percent range.<sup>[58]</sup> However, one can also argue that today's record PCEs in the 12–15 % range, up to 17 % for tandems<sup>[59]</sup> does not stand the comparison with most recent wet-processing technologies like lead-halide-perovskites, which also come with their own environmental burden, justifying research into alternative compositions.<sup>[60]</sup> With that in mind, our research requires a similar amount of work to improve the PCE of our materials, understanding that the state of art of modelling structure-property relationships has been partly disentangled already and that our final objective which is to provide cheap sustainable and flexible electronics is still pending.<sup>[61]</sup>

#### 2. Molecular Glasses in Organic Photovoltaics

#### 2.1. Non-Fullerene Acceptor Molecular Glasses

The first venture from our group into designing and synthesizing molecular glass acceptors for OPV cells involved bay-substituted PDI derivatives 11 a-b,<sup>[46]</sup> where a thiol-functionalized glass was reacted with a 2,7-dibromo-PDI precursor.<sup>[62]</sup> The remaining bromo group could then be substituted with pyrrolidine to afford derivatives 12 a-b, which showed a significantly different absorption maximum (670 nm compared to 570 nm for compounds 11 a-b) (Scheme 4).<sup>[55]</sup> Two imide substituents were selected to



Scheme 4. Molecular structures of compounds 11-12.

compare the impact of steric bulk on photovoltaic performance: bulky 2,6-diisobutylphenyl, and linear n-octyl.

All four compounds showed glass formation with no crystallization on heating or standing, and in all cases, the compounds could form blends with P3HT where the P3HT could be made to crystallize by thermal annealing, but the PDI glass remained amorphous. This is a desirable feature, because it enables the formation of small donor domains without perturbation by the crystallization of the acceptor.

All four PDI glasses studied showed photovoltaic activity in inverted OPV cells with P3HT as donor, with PCE ranging from 0.2 to 0.6% (Table 1). Selected J-V curves of the best devices are shown in Figure 1. Though the PCE

observed were low, several insights could be extracted from this study. Firstly, the fact that the acceptor materials were amorphous did not result in vastly lower performances (values observed with analogous crystalline PDI derivatives as acceptors in the literature are under 1 % as well).<sup>[63,64]</sup> Second, the impact of the steric bulk of the imide groups was pronounced, with both octyl derivatives 11b-12b showing PCE three times higher than that of their 2,6-diisopropylphenyl analogues 11 a-12 a. Third, the performance of the devices with octyl imides 11b-12b increased with increasing PDI-glass fraction, showing that the PDI also contributed to cell performance. Fourth, while the pyrrolidinyl derivatives 12 a-b showed an optimal absorption enhancement because of their complementary absorption spectrum with that of P3HT, the bromo derivatives 11a-b resulted in a more efficient crystallization of P3HT, and therefore the performance of the devices with both groups of acceptors were closely similar.

In our attempts to synthesize non-fullerene acceptors that showed higher photovoltaic performance, a diketopyrrolopyrrole (DPP) glass with a rhodanine group functionalized with a mexylaminotriazine unit (DPP-glass, **13**) was synthesized (Scheme 5).<sup>[47]</sup> In order to be able to establish a comparison between amorphous and crystalline materials, an analogue with an ethylrhodanine group (DPP-Et, **14**) was synthesized as well. It should be noted that while numerous other crystalline DPP derivatives have already been reported in the literature,<sup>[65–68]</sup> the objective in the present case was to compare two analogues with identical chromophores so that the electronics of the acceptors would be as closely similar as possible. As the mexylaminotriazine unit is bonded to the



Figure 1. Current-voltage curves of ITO/ZnO/P3HT: acceptor/MoO<sub>3</sub>/Ag devices with PDI glasses 11–12 as acceptor under illumination with an intensity of 100 mW cm<sup>-2</sup>.



Scheme 5. Molecular structures of compounds 13-14.

rhodanine group through an alkyl linker, it is not likely to impact the steric bulk around the DPP unit or perturb the electronic properties of the chromophore.

The photovoltaic performances of DPP-glass 13 with P3HT as donor proved to be significantly higher than that of PDI glasses 11-12, reaching PCE up to 1.54% in inverted cells and 2.50% in conventional cells. In contrast, ethylsubstituted crystalline analogue 14 yielded maximal PCE of 0.99% in inverted cells and 1.56% in conventional cells (Table 1, Figure 2). In comparison, the highest PCE reported with a DPP derivative with a single DPP unit is 3.30% with P3HT as donor.<sup>[69]</sup> While these results were not the best reported with this chromophore type, the comparative study nonetheless yielded insightful results. In particular, the amorphous derivative consistently yielded performances approximately 50% higher than its crystalline analogue, which is contrary to widespread beliefs in the photovoltaic community. Indeed, while a crystalline material can potentially show higher performances under ideal conditions, in reality the active layer is typically littered with defects, the crystalline domains may not be of ideal size throughout the material, and the interfaces between the donor and acceptor domains may not be properly aligned to facilitate electron transport. In contrast, in amorphous materials, the molecules are oriented randomly, thereby yielding a more homogeneous performance regardless of processing conditions.



**Figure 2.** Current-voltage curves of ITO/ZnO/P3HT:  $acceptor(1:2)/MoO_3/$ Ag inverted devices and ITO/PEDOT: PSS/P3HT: acceptor(1:2)/BCP/Al conventional devices with DPP derivatives **13–14** as acceptor under illumination with an intensity of 100 mW cm<sup>-2</sup>.

#### 2.2. Molecular Glasses as Guest Acceptors in Ternary Blend Cells

Besides molecular glasses being used as principal donors or acceptors in the active layer, they can be used as ternary components within already known crystalline systems.<sup>[70]</sup> Ternary blend OPV cells constitute a simple approach to increase the light harvesting process by using an additional donor or acceptor that provides additional light absorption in areas of the visible spectrum where the donor-acceptor blend absorbs weakly.<sup>[71-73]</sup> This is especially useful with fullerene acceptors, as their absorption in the visible range is weak. The concept in this case is that the amorphous nature of the additional glass-forming component (either a donor or an acceptor) would ensure that it would not disrupt the nanocrystalline morphology of the donor-acceptor blend, instead locating at the interface between domains. One common challenge when adding components to a system is to make sure that each component does not negatively impact the others, and as a result, care must be exercised with crystalline systems to ensure that the ternary component does not disrupt the crystallization of the donor and acceptor into the nanocrystalline domains present in the bulk heterojunction. Alternatively, in some cases, ternary mixtures can forego crystallization altogether, instead yielding an amorphous active layer. For example, both PC<sub>61</sub>BM and PC<sub>71</sub>BM crystallize when blended with quinoxaline donor polymer TQ1, but a TQ1:PC<sub>61</sub>BM:PC<sub>71</sub>BM ternary blend yields a glass-forming fullerene alloy which is thermally stable up to 170 °C.<sup>[74]</sup> While the reported efficiency (4.5%) is lower than that with either pure PC<sub>61</sub>BM (4.9%) or PC<sub>71</sub>BM (7.0%), the devices show higher thermal stability and improved processability.<sup>[75]</sup>

The molecular glasses designed so far by our group for photovoltaics are known to allow the crystallization of other components in the blend without crystallizing themselves, making them suitable candidates as ternary components for OPV cells.

Both pyrrolidinyl-substituted PDI glass 12b and DPPglass 13 were evaluated as ternary acceptors in the wellestablished P3HT:PC61BM system in inverted devices. Both PDI-glass 12b and DPP-glass 13 improved cell efficiency with increasing weight fraction, up to optimal concentrations of 20 wt% for PDI-glass 12b and 15% for DPP-glass 13, resulting in performance enhancements of 38 and 36% relative to the control binary devices, respectively (Table 1, Figure 3). Higher concentrations of ternary acceptors resulted in lower increases in performance due to grainier morphologies. Otherwise, the ternary acceptors were shown to not disrupt the nanocrystalline morphology of the P3HT: PC<sub>61</sub>BM blend, and contribute to the overall absorption of the devices, thereby accounting for their performance enhancement. Furthermore, the long-term stability of the devices was shown to be only slightly lower than that of P3HT: PC<sub>61</sub>BM binary devices.

In addition to organic PV cells, donors or acceptor molecular glasses can be introduced as interfacial layers in PV



**Figure 3.** Current-voltage curves of ITO/ZnO/P3HT:  $PC_{61}BM(1:1)/MoO_3/$  Ag devices in the absence or in the presence of acceptor glasses **12b** or **13** as ternary acceptors under illumination with an intensity of 100 mW cm<sup>-2</sup>.

cells based on inorganic materials, such as perovskites.<sup>[76,77]</sup> One challenge with perovskite-based PV cells is to use materials and processing conditions that are compatible with processing on flexible substrates. In particular, cells using mesoporous TiO<sub>2</sub> processed at high temperatures as electron collecting layer yield significantly higher performances than cells using solution-processed TiO<sub>x</sub> annealed at lower temperatures, but the latter is more compatible with commercial panels.<sup>[78–80]</sup> To compensate for the lower efficiency of TiO<sub>x</sub>-based electron collecting layers, it is possible to incorporate a thin layer of an organic material to improve electron transfer from the perovskite layer to the TiO<sub>x</sub> layer. The addition of a 10 nm layer of PDI glass **11b** improved cell efficiency by 38%,<sup>[81]</sup> which is similar to values reported for the significantly more expensive PC<sub>61</sub>BM.<sup>[82]</sup>

#### 2.3. Fully Amorphous Active Layers

Being able to access both glass-forming donors and acceptors would enable the fabrication of OPV cells where the active layer is entirely amorphous, thereby mitigating the dependence of device performance on processing conditions. In these cases, the donor and acceptor are likely to be blended homogeneously, as opposed to segregated in nanocrystalline domains in crystalline bulk heterojunctions. While the common belief is that phase-segregated nanocrystalline domains are essential for proper device performance, it is nonetheless possible that homogeneously blended components also yield an appreciable photovoltaic performance.

For exploratory purposes, a glass-forming squarylium cyanine derivative (SQ-glass, **15**) was synthesized as donor (Scheme 6). While this constitutes the first time a squarylium



Scheme 6. Molecular structure of compound 15.

cyanine is used as a donor in OPV cells, squaraines are wellknown as donors,<sup>[83]</sup> and squarylium cyanines can be synthesized in significantly higher yields.<sup>[84]</sup> Indeed, SQ-glass **15** could be synthesized from commercial precursors and a triazine glass in two steps and 73 % global yield. As the derivative was symmetrical, two triazine units were introduced, therefore a triazine glass without hydrogen bonding groups (**6**) was used in this case.

SQ-glass **15** was incorporated into inverted cells with either DPP-glass **13** or  $PC_{61}BM$  as acceptor. In the case of DPP-glass **13**, the active layer was completely amorphous. However, with  $PC_{61}BM$ , it was possible to promote the crystallization, and phase segregation, of  $PC_{61}BM$  by thermal annealing, thereby allowing the comparison of the cell performance between the homogeneous and phase-segregated SQ-glass:  $PC_{61}BM$  blends.

Low PCE were obtained in each case, ranging from 0.41 % with DPP-glass **13**, to 0.44 % with homogeneously blended PC<sub>61</sub>BM, to 0.52 % with crystalline PC<sub>61</sub>BM (Table 1, Figure 4). This is likely due to SQ-glass **15** itself being a poor donor, which could be due to either the chromophore, or to the presence of two triazine units that unnecessarily dilute the chromophore.

In any case, the key observation in this study is the fact that the homogeneously blended SQ-glass:PC61BM cell yielded an efficiency only 18% lower than the cell with a phase-segregated blend. This indeed tends to confirm at first the widely accepted theory that phase segregation is crucial for optimal device performance. Technically, the charges from dissociated excitons have to be conducted through different channels in order to limit bimolecular recombination.<sup>[35]</sup> However, it must be noted that with nanocrystalline, phasesegregated systems, conversion efficiency tends to sharply decrease with increasing device size as a result of a higher defect density.<sup>[85,86]</sup> For example, efficiencies up to 5% have been reported with the benchmark P3HT: PC61BM system in small-scale devices (under 1 cm<sup>2</sup>).<sup>[87]</sup> However, commercialscale devices using the same active layer show efficiencies on the order of 1 %.<sup>[88]</sup> Although homogeneous blends with SQ-



**Figure 4.** Current-voltage curves of ITO/ZnO/**15**: acceptor/MoO<sub>3</sub>/Ag devices with DPP glass **13** or  $PC_{61}BM$  (homogeneous: fully amorphous; phase-segregated: PCBM crystals visible by XRD) as acceptor under illumination with an intensity of 100 mW cm<sup>-2</sup>.

glass **15** have not yet been tested with larger cells, it is envisageable that given the random nature of amorphous materials and their lesser dependence on processing conditions, such blends yield more consistent performance independently of device size. This in particular constitutes a very strong motivation to study the concept in greater depth.

To improve the PCE of the fully amorphous devices, the first step would consist in generating more donors and acceptors based on systems known to yield higher PCE in the crystalline state, and perform a thorough screening of donoracceptor pairs to identify the most promising materials. Furthermore, it is likely that if both the donor and acceptor are ambipolar transport materials, the PCE could be enhanced because it would be easier to generate a continuous channel for the charges to reach their respective electrodes. Obviously, the ideal scenario would consist in inducing the formation of nanoclusters of both the donor and acceptor, even in the amorphous phase. This way, the isotropic properties of molecular glasses could be combined with the phase-segregated architecture of bulk heterojunctions, thereby allowing for optimal morphology for both electron and hole transport, and for avoiding defects in the active layer. One potential way to achieve this consists in using orthogonal non-covalent interactions, such as hydrogen bonding or  $\pi$ - $\pi$ stacking, to direct the supramolecular assembly of both active layer materials in the glass. The triazine glasses developed in our group are already adapted for this purpose, as it is possible to use either the series of triazine units with NH groups that can readily form hydrogen-bonded assemblies, or the series with NMe groups that are devoid of hydrogen bond donors.

#### 3. Summary and Outlook

Molecular glasses constitute an appealing alternative to both polymers and crystalline small molecules as active layer materials for organic photovoltaics. Mexylaminotriazines are one class of molecular glasses that shows outstanding glassforming properties, and their structures can be adapted to be easily functionalizable through covalent bond-forming reactions, enabling the fast, efficient, reliable and predictable design of materials for various photonic and opto-electronic applications. This way, time can be invested into optimizing the structures of the chromophores, or electron donor and acceptor moieties, rather than having to rely on trial and error to reach the desired glass-forming properties.

Although the morphology of bulk heterojunctions are most commonly polycrystalline, there are several advantages into introducing amorphous components, including less stringent processing conditions, and more homogeneous behavior independently of processing. The former is important from an industrial viewpoint, because increasing the scale of devices is accompanied by important losses in performance, which are partly attributed to an increase in defect density. The latter is especially important when screening new materials, as mitigating the performance dependence on optimal morphology, which is a result of processing, allows to shift focus on molecular engineering and energy level tuning, which is more easily predictable.

Although still in the early stages of research, the molecular glasses developed in our group have shown to be viable materials for organic photovoltaics. They can be used with crystalline partner materials, and remain amorphous while not impeding the crystallization of the other component. When used with two other crystalline components, they remain amorphous and locate at the interfaces between crystalline domains. Alternatively, a molecular glass donor and acceptor can be used together to yield a fully amorphous active layer that does not recrystallize over time.

While homogeneous blends typically yield slightly lower efficiencies than phase-segregated blends, it is likely that this difference would be mitigated even more when increasing device size, due to the consistent random morphology of amorphous materials. With careful molecular design, it may also be possible to, at least partially, achieve the phase segregation of molecular glasses, even in the amorphous state, through the use of non-covalent interactions to generate supramolecular arrays.

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