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Hole-transporting Materials for Low Donor Content Organic Solar Cells: Charge transport and Device Performance

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ABSTRACT: Low donor content solar cells are an intriguing class of photovoltaic device about which there is still considerable discussion with respect to their mode of operation. We have synthesized a series of triphenylamine-based materials for use in low donor content devices with the electron accepting [6,6]-phenyl-C71-butyric acid methyl ester ($PC_{71}BM$). The triphenylamine-based materials absorb light in the near UV enabling the $PC_{71}BM$ to be essentially the light absorbing organic semiconducting material in the solar cell. It was found that the devices did not operate as classical Schottky junctions but rather photocurrent was generated by hole transfer from the photoexcited $PC_{71}BM$ to the triphenylamine-based donors. We found that replacing the methoxy surface groups with methyl groups on the donor material led to a decrease in hole mobility for the neat films, which was due to the methyl substituted materials having the propensity to aggregate. The thermodynamic drive to aggregate was advantageous for the performance of the low donor content (6 wt%) films. It was found that the 6 wt% donor devices generally gave higher performance than devices containing 50 wt% of the donor.

KEYWORDS: photoexcited hole transfer; photocurrent generation, synthesis, hole mobility, low donor content, Schottky junction.

Introduction

Over the last decade, steady improvement in photoconversion efficiencies (*PCEs*) have been reported for laboratory scale bulk heterojunction (BHJ) organic photovoltaic (OPV) devices.[1] The early improvements

in PCE were achieved through the development of donor materials with smaller optical gaps[2] that were capable of efficient charge transfer to fullerene acceptors and had sufficient charge carrier mobility. Fullerene acceptors can also contribute to light absorption and photocurrent generation via photoinduced hole transfer.[3] In this context, [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₁BM) has significant absorption in the visible and a larger molar extinction coefficient than [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM).[4] Indeed, there have been a number of fullerene-containing OPV devices with a large open circuit voltage (V_{OC}) and high *PCE* even when the donor content was very low [≈ 5 weight percent (wt%)] with respect to normal bulk heterojunction solar cells.[5-11] There have been a number of studies undertaken towards understanding how such devices work. Zhang et al. used low concentrations of 4,4'cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine] (TAPC) blended into a fullerene host and described the solar cells as BHJ Schottky diodes with the BHJ-MoOx interface giving rise to the large opencircuit voltage.[5] They found that at higher TAPC concentrations the device performance decreased, which was ascribed to a decrease in the electron percolation pathways and mobility through the fullerene component.[5] In contrast, Vandewal et al. suggested that based on external quantum efficiency measurements the donor molecules were "well-dispersed" in the fullerene matrix and that the open-circuit voltage was dependent on the interfacial area available for charge carrier recombination.[11] However, if the donor molecules are completely dispersed in the fullerene matrix then the photogenerated holes would not be able to hop through the fullerene phase and be extracted.[12] Recent work by Spoltore et al. has suggested that 6 mol% of the donor in the fullerene is below the percolation threshold and that holes move through the film by tunneling between the donor molecules across a number of fullerenes.[13] However, molecular simulations on the morphology of vapour deposited low donor content solar cells show that when the donor concentration is as little as 5 wt% then based on a hole hopping distance of 1.2-1.5 nm there is a sufficiently interconnected donor network to facilitate hole extraction.[14] Therefore, there are still a number of questions that need to be answered to have a complete picture of how low donor content solar cells operate. To develop a clearer understanding of the photoinduced hole transfer processes and performance in low donor content PC70BM devices, the ideal donor should have the following properties: i) no significant absorption in the visible; ii) a low ionisation potential relative to the acceptor; and iii) the donor should be capable of sufficient hole transport to facilitate charge extraction and avoid bimolecular recombination losses. It has been previously shown that the slow carrier mobility plays an important role in device performance.[15]

Triarylamine-based hole-transport layers have been developed for organic light-emitting diodes,[16] but only a very small selection of these have been studied in the context of photovoltaic devices. In this work, we study four near-UV absorbing dendrimers based on triphenylamines (**Figure 1**) as hole acceptors and transporters for low donor content OPV devices. The triarylamine dendrimers differ in two ways, namely the

number of surface groups (three or six with the latter having increased symmetry) and the type of surface group (alkoxyl or alkyl). We relate their physical properties to the mobilities and show how they can help reveal the charge generation and transport in low donor content devices. OPV devices have been fabricated with donor contents of 6 wt% (low donor) and 50 wt% (normal bulk heterojunction) with PC₇₁BM. A significant increase in the *PCE* was achieved by increasing the PC₇₁BM loading (decreasing the donor content). In these devices charges can only be generated by photoinduced hole transfer as the fullerene is the primary absorber. Finally, we show that the low donor content devices are best not described as Schottky junctions.



Figure 1 Molecular structures of the triarylamine dendrimers

Results and discussion

The triarylamine hole-transporting dendrimers with different surface groups were synthesized using two simple steps based on modified literature methods (Scheme 1 and Supporting Information), specifically an acid catalysed amination followed by a Buchwald reaction. The modified route in Scheme 1 led to much higher yields with good reproducibility for each of the materials in comparison to the previously reported methods that used a Knöevenagel reaction[17] for the first step and an Ullman reaction[18] for the second. The latter approach required high reaction temperatures, long reaction times and afforded hard-to-separate products. The synthesis of **1a-1c** was carried out under mild conditions following the method reported by Müllen *et al.*[19] Concentrated hydrochloric acid was used as the catalyst and at 60 °C the reaction proceeded rapidly as evidenced by fast precipitation of the product. The products were isolated in a pure form via precipitation from methanol, giving yields of 52%, 41% and 42% for **1a**, **1b** and **1c**, respectively. The Buchwald reaction with the required aryliodide gave the desired target compounds in good yields of 82%, 50%, 89% and 82% for **2a**, **2b**, **2c** and **2d**, respectively.



Scheme 1 Synthetic routes for 2a-d: (*i*) conc. aq. HCl (37%), 60 °C for 20 min, 120 °C for 1 h; (*ii*) Pd₂(dba)₃ (5%), *t*-Bu₃PH·BF₄ (10%), NaO*t*-Bu, xylene, reflux, 36 h.

The thermal properties of the materials below their decomposition temperature were characterized by Differential Scanning Calorimetry (DSC). Figure S1 shows the DSC plots for the four materials and Table 1 summarises their thermal behaviour. The as purified 2a was found to have a glass transition temperature (T_g) at 56 °C followed by crystallization at 113 °C, before finally melting at 193 °C. On cooling no thermal transitions were observed at a scan rate of 50 °C/min and on the subsequent scans the behaviour was the same as the one shown in the first scan apart from the crystallization being observed at 108 °C. When all six benzene rings of 2b were substituted with methoxy groups at the para-position only a melt was observed at 200 °C with a subsequent crystallization observed at 143 °C during the cooling scan. For the compound with three methyl groups, 2c, the first scan showed that at a constant heating-cooling rate of 50 °C/min there was an exothermic peak at 100 °C (not observed at scan rates of 10 or 100 °C/min) before the compound melted at 200 °C. The sample was then observed to have a broad crystallization peak on cooling. The thermal behaviour was independent of scan number under the same conditions and the broad exothermic transition suggested that polymorphs of 2c exist, which is consistent with previous reports of 2c having polymorphs [20]. To probe the polymorphism further the heating and cooling rates were varied (Figure S2). By heating the sample slowly (10 °C/min) followed by fast cooling (100 °C/min) (Figure S2a), the compound that was obtained by recrystallization from a dichloromethane/methanol mixture was found to have two melting transitions at 200 °C and 215 °C and the same broad crystallization process centred at 130 °C. Figure S2b illustrates that when fast heating and cooling rates are used (100 °C/min) only a single melt is seen that is a combination of the two processes observed at the slower heating rate. When the cooling rate was decreased to 10 °C/min two different crystallization processes occurred (Figure S2c). 2c has been previously reported to have a Tg at 58 °C [20] but we did not observe such a transition. The six methyl group substituted compound 2d showed crystalline behaviour with a melt at 240 °C and a crystallisation at 219 °C during the cooling scan. In summary, the thermal characteristics show that the molecules with the greater number of surface groups have the greater propensity for aggregation.

Sample -	IP (eV)	Ordical con ^{a} (cV)	T (°C)	$T_{\rm c}$ (°C)	$T_{\rm m}$ (°C)	T_{d}^{b}
	PESA	Optical gap (ev)	<i>I</i> _g (C)			(* C)
2a	5.4	3.4	56	94	193	377
2b	5.3	3.3	-	143	199	398
2c	5.4	3.4	-	130	200/215	360
2d	5.3	3.4	-	219	240	340

Table 1 Energy levels and thermal properties of the materials.

^{*a*}estimated from film absorption and emission;[21] ^{*b*}5% weight loss.

The optical properties of the four compounds in solution and thin film were measured and the results are displayed in Figure 2. The pristine thin films were spin-coated from chloroform solution at a concentration of 20 mg/mL, giving an average film thickness of ~90 nm. The compounds showed similar absorption profiles exhibiting maxima at around 300 nm with onsets at wavelengths less than 400 nm. The fact that the absorption of both the solutions and thin films were in the near-UV region is important for the study of charge generation when blended with the fullerene electron acceptor. Given that standard ITO on glass substrates begin to absorb strongly at around 350 nm the short wavelength absorption of the donors means that there should be negligible contribution to photocurrent generation by electron transfer from the dendritic donors to the acceptor. The type and number of surface substituents was found to have little influence on the absorption of the materials or their solution photoluminescence (PL) spectra. The solution (dichloromethane) PL spectra were featureless with a similar λ_{max} between 420-450 nm. In the solid-state the PL maximum had a slight blue shift (to ≈ 400 nm) but in all cases there was a broad component extending to longer wavelengths, with the latter more pronounced for the methyl substituted compounds, 2c and 2d. The red component of the PL spectra is consistent with aggregate/excimer emission in the solid-state. To provide further evidence for the broad red emission arising from aggregation, 2c was dispersed in a poly(styrene) matrix at loading concentrations of 10 wt%, 20 wt% and 50 wt% and the thin film absorption and PL measured (Figure S3). Poly(styrene) absorbs at wavelengths shorter than 2c and hence has negligible influence on its absorption profile. Figure S3b shows the effect of 2c concentration in poly(styrene) on the relative intensity of the long wavelength component of the emission, which increases upon the increasing 2c loading. Thus the red component of the emission is due to intermolecular interactions in the solid-state. These results indicate that the spin-coated films are comprised of relatively ordered and amorphous regions although the exact proportion of these in the film cannot be determined from the PL spectra. Based on the

thin film PL data, the methyl group containing 2c and 2d appear to have stronger intermolecular interactions (a greater degree of aggregate/excimer emission) than their methoxy substituted counterparts, 2a and 2b, respectively.

b)



Figure 2 Normalised absorption (solid lines) and emission (dotted lines) spectra of (a) 2a; (b) 2b; (c) 2c; (d)2d in solution (dichloromethane) and spin-coated thin films (from chloroform).

The ionization potential (IP) of the dendrimers were determined using Photoelectron Spectroscopy in Air (PESA) with the results summarized in **Table 1**. All the materials possessed IPs of 5.3-5.4 eV, which was suitable for photoinduced hole transfer when blended with $PC_{71}BM$. Finally, before fabricating and testing

a)

solar cells we measured the hole mobilities of the neat materials using space-charge-limited-current (SCLC) measurements using a unipolar device architecture. The hole mobilities as a function of electric field are shown in **Figure S4** with the data at an electric field of 1×10^{-5} V/cm (which is comparable to short-circuit conditions) summarised in **Table 2**. The SCLC was analyzed using the Poole-Frenkel model, which is an established method to quantify field-dependent mobilities of organic semiconductors.[22] Each material exhibited a field-dependent mobility with that for **2c** and **d** more pronounced than **2a** and **b**. Furthermore, it can be clearly seen that the methoxy substituted materials had a hole mobility an order of magnitude greater than their methyl counterparts. The lower hole mobility and greater field dependence for the methyl substituted materials implies that the films have a greater proportion of traps, which is consistent with the film PL spectra that had a greater proportion of aggregate/excimer emission.



d)

b)

c)

a)



Figure 3 Current density-voltage curves (a, b) under simulated AM1.5G solar illumination and the corresponding EQEs (c, d) of devices with the active layers comprising dendrimer **2a**, **2b**, **2c** or **2d**:PC₇₀BM blends with dendrimer content of 6 wt% or 50 wt%.

Next, we prepared films with the donor materials blended with PC₇₁BM as the electron acceptor. Solutions were prepared with the donor material at two different weight percents. The 6 wt% device was defined as low donor content in line with previously reported work, with the 50 wt% being representative of a standard bulk heterojunction device. Atomic Force Microscopy was used to measure the surface topology of the 6 wt% films, which were all found to be similar (Figure S5). With all solution processed devices there is an interesting question as to whether the ratio of the materials in the processing solution is the same as in the final film. We have previously shown that for a low donor dendrimer: PC₇₁BM device the ratio of donor and acceptor in the film was similar to that in the processing solution.[10] To confirm that this was the case for the materials of this study we used X-ray reflectometry to determine the wt% of the donor in the films for 2a following the previously reported method.[10] We found that the 6 wt% solution gave films with a 8 wt% 2a concentration and the 50 wt% solution led to films with 54 wt% of the donor. That is, within experimental error the concentration in solution and the films were similar and for simplicity we will use the wt% in the processing solution throughout the discussion. Figures 3(a-d) depict current density-voltage (J-V) characteristics and external quantum efficiency spectra (EQE) for devices comprising an active layer of 2ad:PC₇₁BM, at donor concentrations of 6 wt% and 50 wt%, with device performance parameters summarized in Table 2. There are two important trends that can be seen from the data. First, apart from the 2b:PC₇₀BM combination, the 6 wt% devices had PCEs more than double that of the 50 wt% devices, and second, the blends containing the methyl substituted dendrimers on average performed better than their methoxy substituted counterparts. In both cases the improvement is mainly due to an increased J_{SC} . The increased J_{SC}

for the 6 wt% films makes sense in that it is the $PC_{71}BM$ that is the primary absorber and hence makes up a greater proportion of the low donor content films in comparison to the 50 wt% blends.

 Table 2 Mobilities measured by SCLC for neat films and device performance at the two different donor concentrations.

Material	${\mu_{ m hole}}^a$ (cm ² /Vs)	Blends ^b	V _{OC} (V)	$J_{\rm SC}$ (mA/cm ²)	FF (%)	<i>PCE</i> (%)
2a	4.0×10 ⁻⁶	6 wt%	0.72±0.01	3.50±0.10	34.5±0.4	0.90±0.02
		50 wt%	0.66 ± 0.07	1.0±0.03	30.0±4.0	0.20 ± 0.04
2b	7.3×10 ⁻⁶	6 wt%	0.62±0.02	2.40±0.05	32.2±1.0	0.50±0.02
		50 wt%	0.67 ± 0.02	2.10±0.04	38.0±1.0	0.50±0.10
2c	3.2×10 ⁻⁷	6 wt%	0.75±0.01	3.80±0.10	39.6±1.9	1.10±0.10
		50 wt%	0.82 ± 0.02	1.90±0.20	29.0±1.0	0.40 ± 0.10
2d	7.2×10 ⁻⁷	6 wt%	0.79±0.02	4.40±0.10	37.4±1.0	1.30±0.05
		50 wt%	0.54 ± 0.04	0.50±0.10	33.0±2.0	0.10±0.03

^{*a*} neat film by SCLC at an electric-field of 1×10^{-5} V/cm using the low frequency dielectric constants determined from dark-CELIV measurements. The SCLC analysis used a built-in voltage of zero based on the symmetry of the *J-V* characteristics in forward and reverse bias; ^{*b*} device architecture: ITO/MoO_x (10-30 nm)/ dendrimer (wt%):PC₇₁BM /Ca (20 nm)/Al (60 nm).

The performance of BHJ OPV devices has been shown to be dependent on the slower charge carrier mobility, being ascribed to the opposite charges being confined to different phases and the increase in entropy of having the charge carriers separated.[15] Based on the hole mobilities of the neat films it might be expected that the methoxy substituted dendrimers would have the better device performance. However, this is clearly not the case with methyl derivatised dendrimers giving rise to the best performance. It is important to note that the mobilities measured on neat films do not necessarily translate into blend device performance. In order to understand the charge transport in the most efficient solar cells (6 wt%) we used resistance dependent photovoltage (RPV) to measure the mobilities in devices containing **2a** and **2c** as examples of the methoxy and methyl containing donor materials. RPV is similar to the time-of-flight experiment but utilizes a range of load resistances, allowing determination of both the faster and slower carriers in a single experiment.[23,24] In essence, at the largest load resistance (1 MΩ), the voltage build-up shows the movement of the photogenerated charges to the extracting electrodes while the voltage saturation with increasing load resistance indicates the extraction of all charges from the device. By knowing the film

thickness within the device, the photocarrier mobility can be readily estimated from the transit time. Figure 4 shows RPV transient signals as measured on devices fabricated from 2a and 2c with 6 wt% donor content, which reveal significant differences in the extraction dynamics in these two devices. For 2a, two extraction shoulders appear in the transient signals corresponding to the extraction of electrons ($\sim 1 \times 10^{-3} \text{ cm}^2/\text{Vs}$) and holes ($\sim 6 \times 10^{-7} \text{ cm}^2/\text{Vs}$) on different timescales. A mobility of $\sim 1 \times 10^{-3} \text{ cm}^2/\text{Vs}$ is consistent with the electron mobility previously reported for $PC_{70}BM[12]$ and the high fullerene content in the low donor content films. In contrast, for devices made from 2c, the second shoulder is absent, which would suggest that the electrons and holes are extracted on similar timescales due to comparatively high and balanced mobilities ($\sim 1 \times 10^{-3}$ cm^2/Vs). Thus the low content donor device comprising the methyl containing dendrimer 2c has a hole mobility several orders of magnitude greater than the devices prepared from the methoxy-substituted dendrimer 2a. This might explain the higher FF and larger PCE for the 2c devices compared to 2a. However, given the relatively low FFs in general, it is likely that there are other factors also strongly impacting the device performance. We also note that the hole mobility in the 6 wt% 2c:PC₇₀BM is orders of magnitude larger than the hole mobility of the neat films of 2c. To investigate this behaviour further we have recorded RPV transients for neat films of 2c (Figure S6). The neat films were found to have more dispersive transport then the corresponding blend. Although a significant fraction of the maximum photovoltage was produced after 100 ns (i.e., on similar timescales than observed in the blend), the charge extraction continued to occur by discharge through the external circuit on timescales $>10^{-3}$ s. In fact, a proportion of the charges were found to be trapped with timescales of more than 100 ms. Evidence for the trapped charges at longer timescales be seen from the overall decrease of the magnitude of the photovoltage (Figure S6) of transients recorded at a repetition rate of 10 Hz with respect to the first transient. The decrease in the photovoltage is a result of accumulated charges in the active layer that recombine with photogenerated charges from subsequent laser excitations. Thus, these results indicate that in the 6 wt% 2c:PC70BM blend the hole transport becomes less dispersive than the neat film and that the film morphology changes to enable for efficient hole extraction. Although it is not possible to experimentally determine the exact distribution of the donor substituents within the fullerene matrix of these low donor content cells, the work of Lee et al. indicates that even at 6 wt% of the donor in the fullerene there should be sufficient interconnected pathways of donor material between the electrodes to enable hole extraction.[14] Our results showing an improvement in hole mobility of the blend relative to the neat film is not unusual. Improvements in hole mobilities relative to neat films of materials have been previously reported for polymer: fullerene blends [25,26]. In the case of a MDMO-PPV:fullerene blend, the authors found that the hole mobility in the MDMO-PPV phase increased by more than two orders of magnitude compared to the neat polymer film mobility.[26] The lower mobility in the neat material was attributed to a ring-like two-dimensional morphology, with the addition of the

fullerene resulting in a enhanced intermolecular interactions of the polymer chains leading to a better percolation pathway and improved charge transport between the molecules.



Figure 4 Phototransient signals at different load resistances (1 Ω to 1 M Ω) recorded on devices with 6 wt% donor content of a) 2a and b) 2c using resistance dependent photovoltage (RPV). The extraction of holes is orders of magnitude slower in devices with 2a compared to devices with 2c.



c)



Figure 5 Mott-Schottky plots for solar cells made of 6 wt% of a) **2a**, b) **2b**, c) **2c** d) and **2d** in PC₇₀BM, measured using a triangle voltage pulse length of 100 μs at a frequency of 5 Hz in the dark. The solid lines serve as a guide to the eye.

In the final part of the study, we measured the capacitance versus voltage characteristics using dark-CELIV[27] for neat films and devices comprising 6 wt% of 2a, 2b, 2c or 2d blended with PC70BM to investigate the characteristics of junctions. Figure 5 shows Mott-Schottky plots for the 6 wt% devices and it can be clearly seen that the capacitance does not change from, -1.0 V to near V_{OC} . The sharp change in slope near the V_{OC} is a result of the change in chemical capacitance due to charge injection at flat band conditions and cannot be used to calculate the equilibrium charge carrier density. We note that the Mott-Schottky analysis cannot be applied to quantify equilibrium charge carrier densities below a certain threshold, [28,29] which based on the thickness of the devices is 1×10^{16} cm⁻³/s. The reason for this is that the capacitance in materials with a low doping concentration is dominated by the amount of injected charge from the contacts and/or photogenerated charge (giving rise to a chemical capacitatance). Although, the Mott-Schottky analysis does not allow a reliable estimation of the equilibrium charge carrier density in the devices, it is clear that these devices cannot be considered as classical Schottky junctions as otherwise the $C^{2}(V)$ plot would have a slope that corresponded to the change of the depletion width and resulting capacitance with applied bias. Therefore, Figure 5 indicates that the built-in field of these low donor content solar cells drops evenly across the active layer. We also note that the variation in absolute values of C^{-2} for the different blends arises from differences in the dielectric constant and the thicknesses of the BHJ films. By knowing the thickness of the BHJ films (d) and the device capacitance (C) and area from the dark-CELIV measurements, we calculated the dielectric constant using the equation $C = \frac{\varepsilon \varepsilon_r}{d} A$, where ε and ε_r are the absolute and relative dielectric constants. By using the average capacitance, the low frequency dielectric constant ε_r was determined to be

4.1, 4.3, 3.1, and 2.8 for neat films of **2a**, **2b**, **2c**, and **2d**, and 3.0, 3.8, 3.9, and 4.5 for the **2a**:PC₇₀BM, **2b**:PC₇₀BM, **2c**:PC₇₀BM and **2d**:PC₇₀BM blends, respectively. The low frequency dielectric constants of the 6 wt% blends are of similar magnitude reported for [6,6]-phenyl-C61-butyric acid methyl ester,[30] which along with the electron mobilities indicates that blending small amounts of donor does not have a dramatic effect on the bulk electronic properties of the fullerene host. In the final part of the analysis we determined the ideality factor (n) of the devices. Classical Schottky junctions have n = 1,[31] and hence an ideality factor significantly greater than 1 implies that devices do not Schottky diode character. The ideality factors (n) were determined from the dark *J*-*V* characteristics for the linear region within the voltage range of 600-800 mV (see **Figure S7**) using the equation $J = J_0 \exp(\frac{qV}{nkT})$. The ideality factors, n, were found to be 1.7, 1.4, 1.5 and 1.7, for **2a**, **2b**, **2c** and **2d**, respectively, which are all significantly larger than that expected for a simple Schottky diode.

In conclusion, we have studied a series of triphenylamine-containing hole-transporting materials with low ionisation potentials and large optical gaps. Changing the surface decorating groups from methoxy to methyl caused minimal perturbation of the optical and electronic properties of the material. However, the different surface groups led to different levels of aggregation in the thin films. In neat films the methyl substituted materials had a greater propensity to aggregate leading to hole mobilities an order of magnitude lower than the methoxy derivatised materials. When blended with $PC_{70}BM$ the propensity for the methyl substituted materials to interact was found to be advantageous leading to higher hole mobilities in low donor (6 wt%) content solar cells and overall higher efficiencies. The low donor content BHJ devices were found not to operate by a classical Schottky junction mechanism but rather the light being mostly absorbed by the $PC_{70}BM$ with the current generated by photoinduced hole transfer.

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- Efficient synthesis a series of triphenylamine-based near UV absorbing materials.
- Propensity of the donor materials to aggregate was found to be surface group dependent.
- Photocurrent generated by hole transfer from the photoexcited PC₇₁BM to the triphenylamine-based donors.
- The thermodynamic drive of the donor to aggregate was advantageous for the performance of the low donor content (6 wt%) films.
- It was found that the 6 wt% donor devices generally gave higher performance than devices containing 50 wt% of the donor.