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Synthesis of push-pull triarylamine dyes containing 5,6-difluoro-2,1,3-benzothiadiazole units by direct arylation and evaluation as active material for organic photovoltaics

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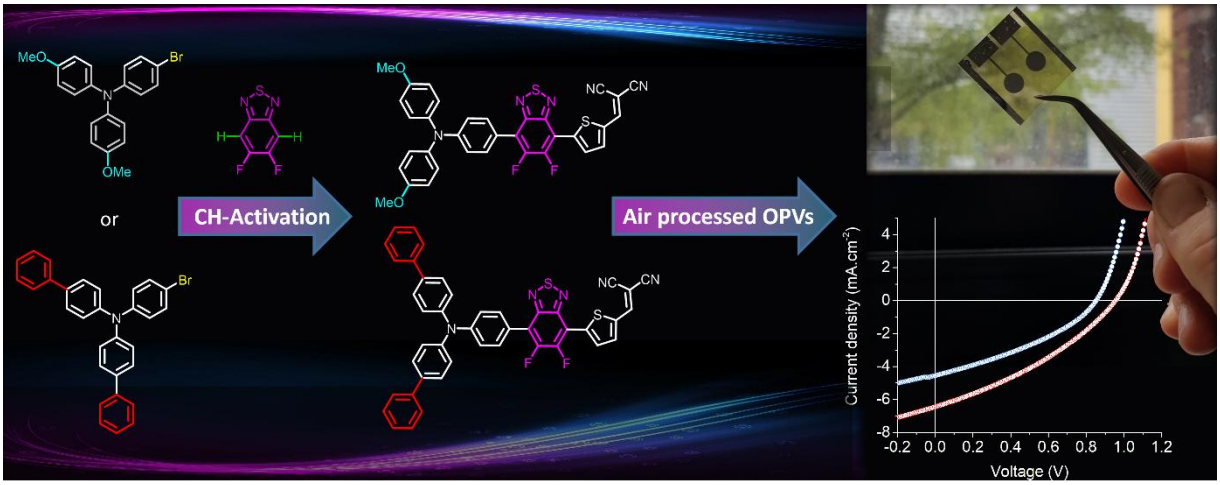


Abstract: Two push-pull molecules involving a triarylamine donor unit connected to a dicyanovinyl acceptor moiety by a difluorobenzothiadiazole-thienyl block have been synthesized. In order to simplify the synthesis, avoid intermediate halogenation reactions and the formation of toxic organometallic by-products, building blocks were connected by direct (hetero)-arylation. The optimization of the experimental conditions of the coupling reactions is thus reported herein as well as the preliminary evaluation of the potential of the target compounds as active material in simple air-processed organic solar cells.

1. Introduction

During the past two decades, the synthesis of active materials for organic solar cells (OSCs) has generated a considerable research effort.[1,2,3] The development of specifically designed conjugated polymers combined with the most recent non-fullerene acceptors has progressively led to OSCs with power conversion efficiencies (*PCE*) approaching 20 %, *ie*, close to those of silicon solar cells.[4] Besides stability, the synthetic complexity, cost and scalability of active materials still remains a major problem for chemists involved in the development of active OPV materials.[1,5] The introduction of molecules with unequivocal chemical structure as a possible alternative to polydisperse conjugated polymers around 2005 has represented a first attempt to address the problems of the cost and scalability of donor materials for OSCs.[6,7,8] However, with a

few exceptions, the synthesis of most of these molecular donors (MDs) resorts to transition-metal-catalyzed C–C cross-coupling reactions.[9,10] This strategy implies the halogenation and functionalization of complementary building blocks by organometallic functional groups. In recent years the direct arylation of C-H activated aromatic or heteroaromatic moieties has emerged, as an appealing alternative to conventional organometallic coupling reactions.[3,11,12] Although high conversion yields can be reach by means of careful optimizations of the reaction conditions, this method has been proven to be perfectly geared for the preparation of polymer and molecular donor materials. For instance, the synthesis of the triarylamine based push-pull **TPA-T-DCV**, (Figure 1) flagship of our group, was recently simplified by the use of the C–H activation of the commercially available 2-Thiophenecarboxaldehyde.[13] Obtained at gram-scale in only two steps from cheap commercially available starting materials, **TPA-T-DCV** presents interesting potentialities as donor material in planar and co-evaporated bulk heterojunction OSCs. These promising first results paved the way to a myriad of structural variations on both the donor (D) and acceptor (A) constitutive blocks with the double objective of a better structure-properties rationalization and optimization of the photovoltaic performances.[8,14,15,16] As shown by Wong and coworkers, the insertion of electron deficient (hetero)aromatic moiety such as benzothiadiazole (BzT) between the arylamine (D) and the dicyanovinyl group (A) represents a particularly interesting approach to finetune the ground- and excited-state characteristics of the D-A system.[17] However, the use of the BzT building generally requires the use of harsh electrophilic halogenation conditions leading to moderate yields, mixtures of products and/or unstable intermediates.

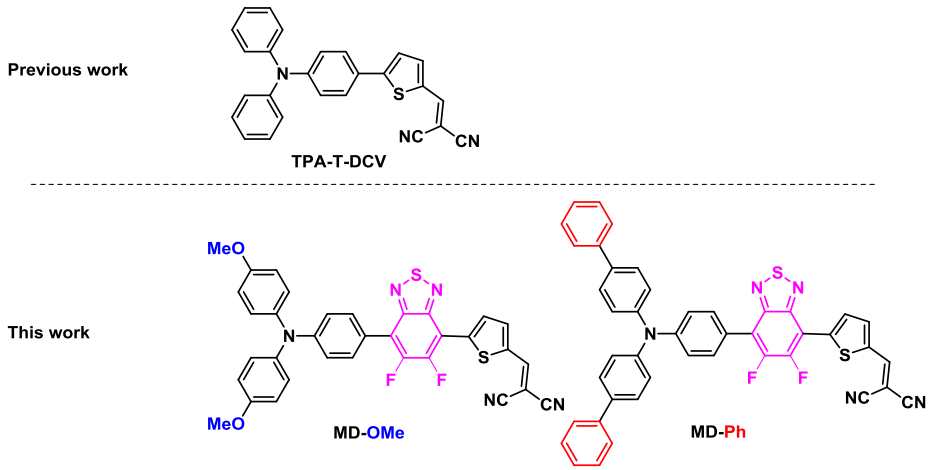


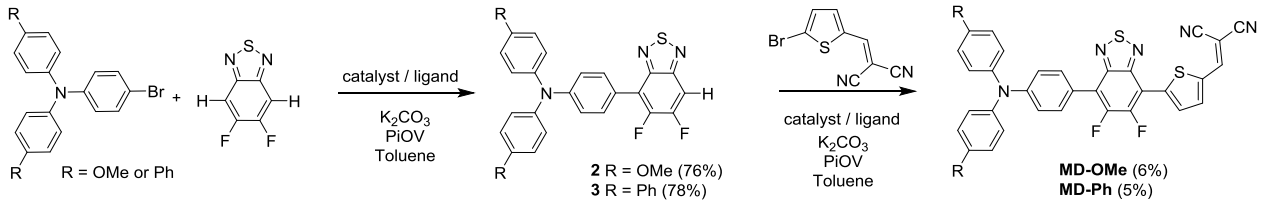
Figure 1. Structure of the early reported **TPA-T-DCV** and the two arylamine based push-pull studied herein, namely **MD-OMe** and **MD-Ph**

In this context, direct (hetero)-arylation appears to be a method of choice to overcome these synthetic problems. Marder and co-workers, have already reported the synthesis of symmetrical and unsymmetrical diaryl flanked 5,6-difluoro-2,1,3-benzothiadiazole (**BT2F**) derivatives using this methodology.[18,19] However considering that difluoro derivative have never been prepared as active materials for organic photovoltaics, we report herein the synthesis, characterization and evaluation of the two push-pull derivatives illustrated in Figure 1. Hence, two different

triphenylamine blocks were used to assess their impact on the electronic and charge transport properties of the molecules and therefore their photovoltaic efficiencies. While the methoxy groups of **MD-OMe** is expected increase the donor strength of the triphenylamine block, the two biphenyl side groups of **MD-Ph** were recently found to significantly increase the hole-mobility of some arylamine based D-A materials.[20]

2. Results and discussion.

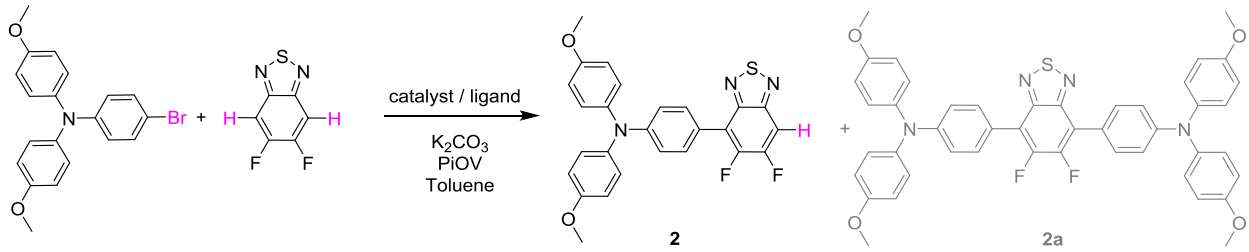
Both push-pull were prepared according to the initial synthetic route depicted in Scheme 1.



Scheme 1. Synthetic route to **MD-OMe** and **MD-Ph**

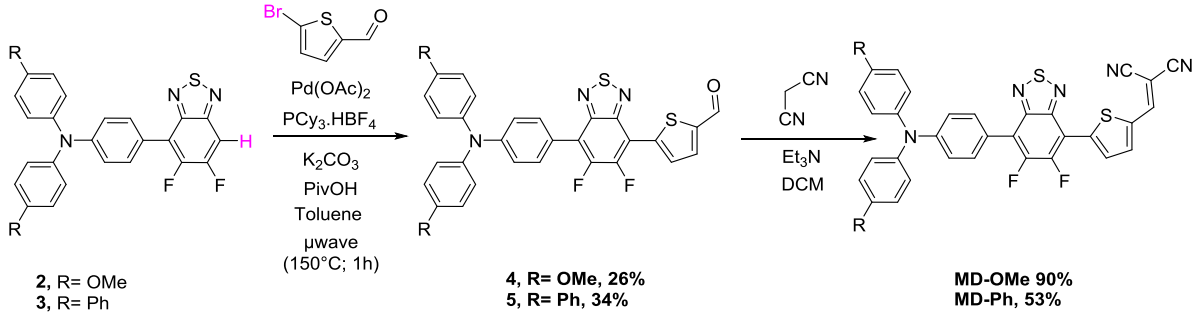
Coupling conditions to afford arylamine functionalized unsymmetrical 5,6-difluoro-2,1,3-benzothiadiazole derivatives **2** and **3**, were first carried out and optimized with the 4-bromo-N,N-bis(4-methoxyphenyl)aniline. As shown in Table 1, the first attempt was performed in presence of Palladium(II) acetate and tri-tert-butylphosphonium tetrafluoroborate ($PtBu_3.HBF_4$) under conventional oil bath heating (entry 1).

Table 1. Reactions conditions used for the coupling of 4-bromo-N,N-bis(4-methoxyphenyl)aniline and **BT2F**



Entry	OMe-Br (eq)	Catalyst (mol %)	Ligand (mol %)	Heat source, temp./time	2 (% yield)
1	1.0	$Pd(OAc)_2$	$P^tBu_3.HBF_4$	Oil bath 120°C; 16h	20%
2	0.5	$Pd(OAc)_2$	$P^tBu_3.HBF_4$	Oil bath (120°C; 16h)	33%
3	0.5	$Pd(OAc)_2$	$P^tBu_3.HBF_4$	μ-wave (150°C; 1h)	36%
4	0.5	$Pd(OAc)_2$	$P(OMePh)_3$	μ-wave (150°C; 1h)	40%
5	0.5	$Pd(OAc)_2$	$PCy_3.HBF_4$	μ-wave (150°C; 1h)	76%

Despite operating in relatively diluted conditions, only moderate yields were obtained mainly because of the major formation of the symmetrical arylamine end capped derivative (**2a**). The reduction of the number of equivalents of bromo derivative by a factor of two results in a slight improvement of the conversion yield (entry 2).In parallel, the replacement of the conventional oil bath by microwave irradiation (entry 3) leads to a further slight improvement of the yield but considerably shortens the reaction time. One hour of irradiation appears as a good compromise between the consumption of the starting material and the formation of the symmetrical by-product (**2a**). Afterwards, the initial catalytic coupled was modified by replacing the tri-tert-butylphosphonium tetrafluoroborate either by the tri(*o*-tolyl)phosphine (entry 4) or the tricyclohexylphosphine tetrafluoroborate (entry 5). While similar conversion rates were monitored with the neutral ligand (entry 4), a descent synthetic yield reaching almost 80% was achieved with the bulkier charged analogue (entry 5). Applied to the biphenyl derivative, these conditions led to the target unsymmetrical 5,6-difluoro-2,1,3-benzothiadiazole based analogue **3** in similar good yields (78%). Each monoarylated products were then subsequently engaged in another cross-coupling reaction with the 2-bromo-5-(2,2-dicyanovinyl)thiophene. Even if the unsymmetrical functionalization of the **BT2F** core by direct arylation was successfully operated with electron rich moieties, low yields were achieved mainly due to the mild reactivity of the halogenated thiophene, that appeared too deactivated by the dicyanovinyl group. Consequently, and as compromise between reactivity and extra synthetic steps, carbaldehyde functionalized unsymmetrical 5,6-difluoro-2,1,3 benzothiadiazole derivatives **4** and **5** were prepared by coupling **2** and **3** with the 5-bromothiophene-2-carbaldehyde respectively (Scheme 2).



Scheme 2. Second Synthetic route considered to **PP-OMe** and **PP-Ph** through a Knoevenagel reaction

Though still modests, synthetic yields achieved were nonetheless significantly improved and are in consistency with early reported results.[18] As a further step toward simplification, attempts to prepare these carbaldehyde derivatives by a one-pot like method were thus carried out. To do so, **BT2F** was first reacted with bromo arylamine before adding the 5-bromothiophene-2-carbaldehyde to the reaction mixture. After a second round of microwave irradiation, carbaldehyde **4** and **5** were successfully isolated with synthetic yields similar to those achieved with the above described two-step procedure. Finally, the later compounds were engaged in a Knoevenagel reaction with malononitrile to afford the corresponding final push-pull molecules. Despite full conversion confirmed in both cases by TLC, the biphenyl derivative was isolated in lower yield due to a limited solubility at room temperature, resulting in a strong interaction with the silica gel. The identity and purity of the final compound was confirmed by NMR spectroscopy and mass spectrometry (see SI).

Figure 2 shows the UV-Vis absorption spectra of the two compounds in dichloromethane (DCM) and as thin film on glass.

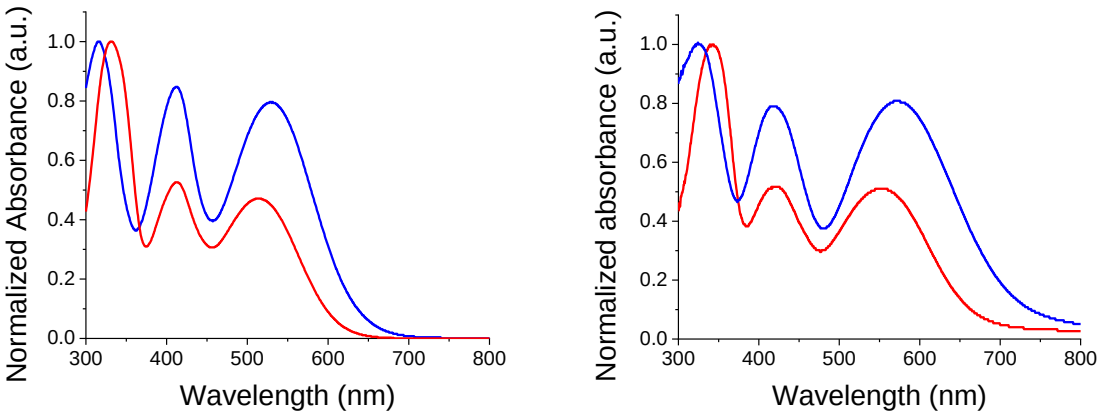


Figure 2. UV-Vis absorption spectra of **MD-OMe** (blue) and **MD-Ph** (red) in DCM (left) and as thin films on glass (right).

The spectrum of both compounds shows three successive absorption bands with maxima at 332, 413 and 513 nm for the biphenyl compound **MD-Ph** in solution. Replacement of the biphenyl by a methoxy group produces, as expected, a small bathochromic shift of the maxima at longer wavelength (*ca* 14 nm) reflecting the higher electron donor effect of the methoxy group compared to a phenyl ring. This behavior results in a reduction of the optical bandgap estimated from the low-energy absorption onset of thin films from 1.86 to 1.68 eV. Comparison of the spectra of the two compounds shows that the introduction methoxy groups on the TPA block also increases the molar absorptivity of the visible absorption bands by almost a factor of two (Table 2).

Table 2. Optical Data gathered from CH_2Cl_2 solutions and on thin films spun casted on glass sheets

Molecule	λ_{abs}^{max} solution (nm)	ε (M^{-1} cm^{-1})	λ_{abs}^{max} thin film (nm)	E_g^{opt} (eV)[a]	HOMO (eV)[b]	LUMO (eV)[a]
	315	51800	325			
MD-OMe	412	44100	421	1.68	-5.43	-3.75
	527	41100	571			
	332	42900	343			
MD-Phe	413	21900	423	1.86	-5.64	-3.78
	513	20200	552			

[a] estimated from the low-energy absorption onset of thin films ; [b] determined by photoelectron spectroscopy in air (PESA) ; [c] LUMO = HOMO-E_g^{opt}

While the UV-Vis absorption spectrum of **TPA-T-DCV** and many of its parent systems usually exhibits a single transition in the visible region, attributed to an internal charge transfer (ICT) from the TPA moiety to the DCV group, the spectra of **MD-OMe** and **MD-Ph** shows two distinct intense absorption bands in the 400-600 nm region. In order to get further insights on this

question, ground-state density-functional theory (DFT) geometry optimizations and density-functional theory (TD-DFT) calculations were carried out using B3LYP/6–311G* basis sets (see SI).

As expected, these experiments first confirmed the ICT nature of the low energy contributions. Assigned to a HOMO->LUMO transition, calculations indeed showed that the electronic density of the HOMO levels is mainly localized on the arylamine moiety while the LUMOs are on the benzothiadiazole/DCV blocks (Figure 3).

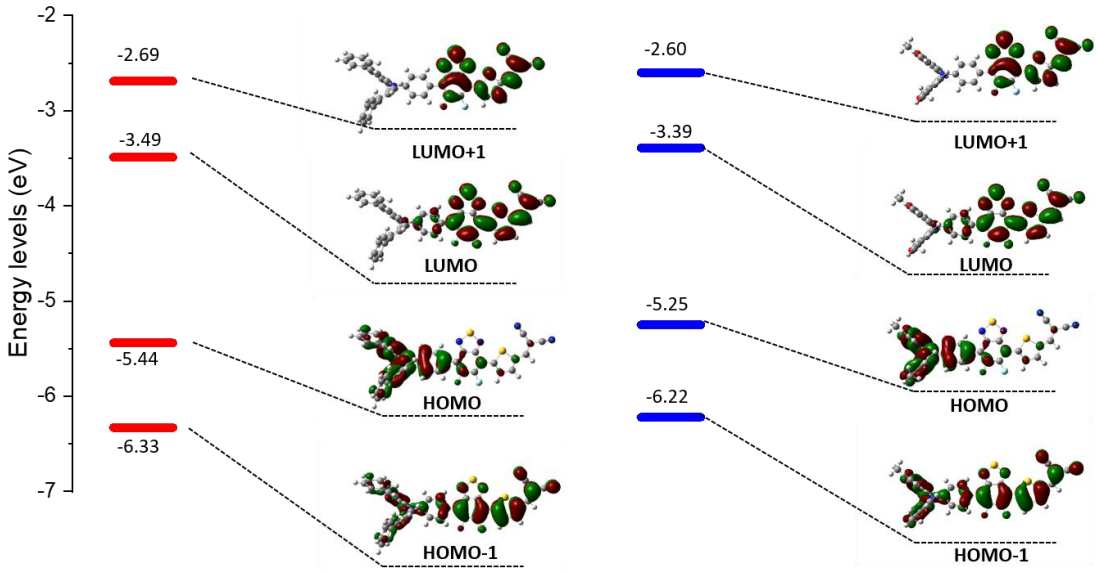


Figure 3. Optimized geometries and computed energy levels of **MD-Ph** (left) and **MD-OMe** (right)

The absorption bands at *ca* 400 nm, were also found to have a charge-transfer character since they predominantly arise from a HOMO-1->LUMO transition (see SI). Moreover, the band gap reduction induced by the electron-donating methoxy groups (**MD-OMe**) compared to simple phenyl rings was found to originate from the significant destabilization of the HOMO level exceeding by far that of the LUMO (Δ_{HOMO} = 0.19 eV *vs* Δ_{LUMO} = 0.10 eV). Hence, photoelectron spectroscopy in air (PESA) measurements were subsequently performed and HOMO levels of -5.43 eV and -5.64 eV were calculated for **MD-Ome** and **MD-Ph** respectively. Once cross-tabulated with UV-visible experiments, the corresponding LUMO levels were simply calculated by adding the optical band gap (film spectra) to the HOMO values thus confirming, as depicted in the figure 4, the computed predictions.

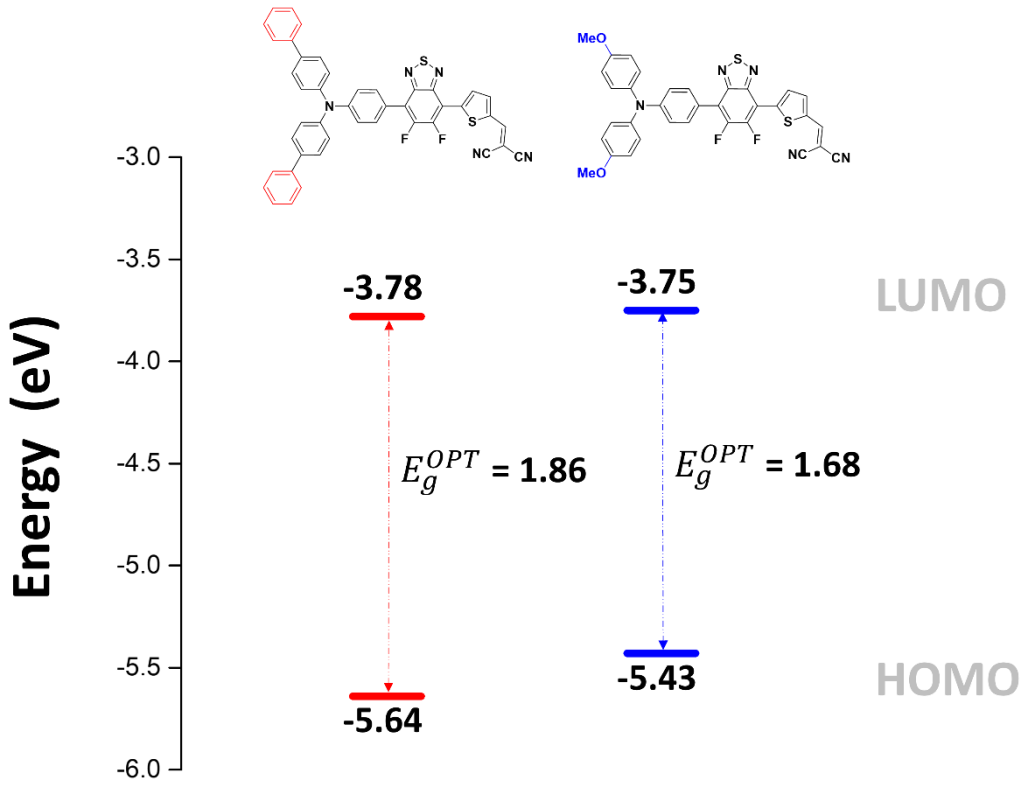


Figure 4. Energy level diagram estimated in solid state from PESA and UV-visible experiments

Designed as potential donor molecular systems for organic solar cells, such difference in HOMO level might have a significant impact on the photovoltaic parameters, in particular on the open circuit voltage (V_{oc}). Consequently, simple air-processed bulk heterojunction (BHJ) solar cells using [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) as electron acceptor material were fabricated. Active layers with different donor: acceptor (D/A) weight to weight (w/w) ratios were processed in air from chloroform solutions, and embedded in devices of architectures ITO/PEDOT:PSS/active layer/Ca/Al. The photovoltaic data measured under AM 1.5 simulated solar light illumination (100 mW·cm^{-2}) are gathered in Table 3.

Table 3. Photovoltaic data measured on 28mm^2 solar cells under AM 1.5 simulated solar light illumination at 100 mW·cm^{-2}.

Molecular Donor	D:A ratio (w/w)	Voc (V)	Jsc (mA/cm²)	FF	PCE (%)
Ome-BT2F-DCV	1:1	0.71	-3.18	0.33	0.74
Ome-BT2F-DCV	1:2	0.85	-4.55	0.35	1.35
Ome-BT2F-DCV	1:3	0.77	-4.73	0.33	1.20
BP-BT2F-DCV	1:1	1.01	-4.56	0.33	1.52
BP-BT2F-DCV	1:2	1.01	-5.47	0.34	1.88
BP-BT2F-DCV	1:3	0.96	-6.43	0.34	2.09

The best power conversion efficiencies, of 1.35% and 2.09%, were reached with a 1:2 and 1:3 D/A ratio for **MD-OMe** and **MD-Ph** based devices respectively . Comparison of their corresponding current to tension (J-V) curves revealed that the better efficiency recorded in **MD-Ph** based OSCs mainly e from their higher short circuit current (Jsc) and open circuit voltage (Voc) values (Figure 5).

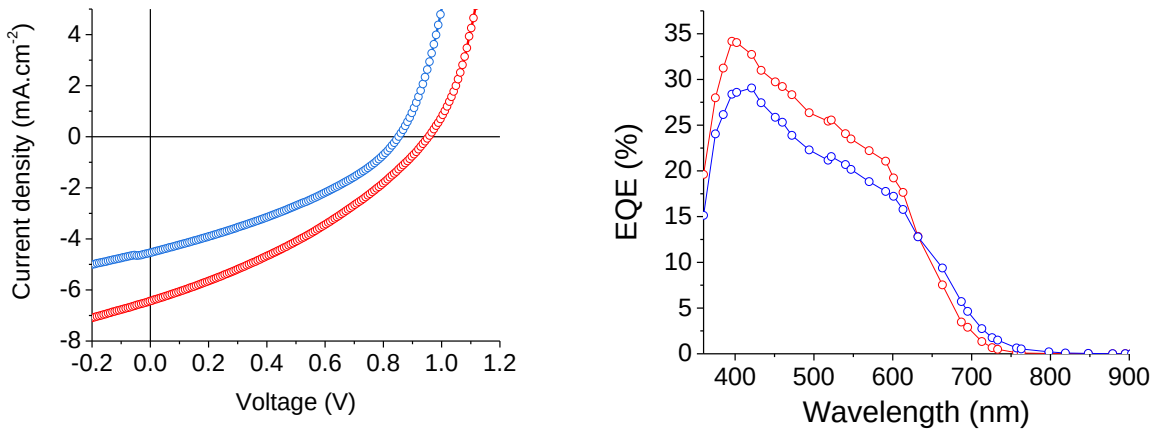


Figure 5. Current density–voltage characteristics and EQE spectra of the best **OMe-BT2F-DCV** (blue) and **Be-BT2F-DCV** (red) based organic solar cells.

While the latter parameter (Voc) can be correlated to the deeper HOMO level of the biphenyl derivative, **MD-OMe** was nonetheless characterized by better absorbing properties in the visible range. Interestingly and in agreement with the recorded Jsc values, external quantum efficiency measurements performed on the best devices also highlighted an improved contribution of the biphenyl derivative to the photocurrent compared to its methoxy counterpart (Figure 5). Hence, in an attempt to rationalize these results, morphologies of the active layers were first probed by atomic force microscopy (AFM). As illustrated in figure 6, smooth surface topographies with similar root mean square (RMS) parameters of *ca* 0.6 nm were observed in both cases, (Figure 7).

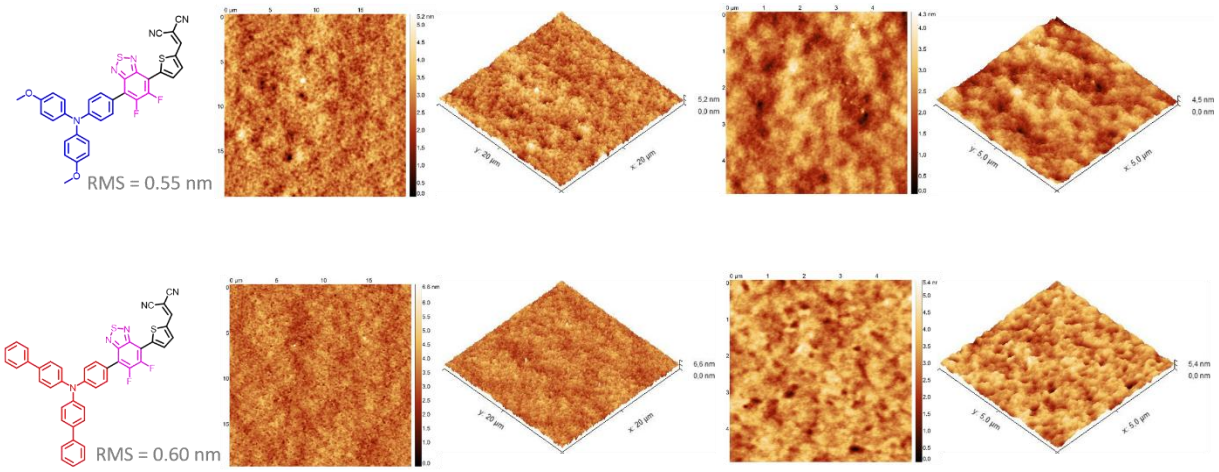


Figure 7. AFM phase images (20x20 and 5x5µm) of optimized **OMe-BT2F-DCV** and **Be-BT2F-DCV** based active layers.

Nonetheless, **MD-Ph/ $PC_{71}BM$** blend exhibits nano domains of smaller size than those observed with the methoxy derivative which can be the harbinger of a better biphenyl induced self-organization of the donor molecule which can, in turn, be beneficial for the charge transport properties and therefore the *Jsc* parameter.
Consequently, both optimized active layers were subsequently embedded in hole-only devices of architecture ITO/PEDO:PSS/donor/Au. Through the use of the space charge limited current (SCLCs) method, hole mobilities of *ca* 7.3×10^{-5} and 8.3×10^{-4} $cm^2 V^{-1} s^{-1}$ were measured for **MD-OMe** and **MD-BP** respectively (see SI). Consequently, this order-of-magnitude difference might compensate the lower absorbing properties of the active layer and contribute to the higher Jsc value delivered by the **MD-BP** based devices.

3. Conclusion

In summary, two new triphenylamine based push-pull molecules containing 5,6-difluoro-2,1,3-benzothiadiazole units have been synthesized. In order to simplify the synthesis procedure and limit the formation of potentially toxic by-products, two major steps of the synthesis were performed using optimized direct (hetero)-arylation conditions. As a step towards simplification, the synthetic route was further shortened by the use of a “one-pot” procedure without modification of the catalytic system nor purification of intermediates. The analysis of the electronic properties of the two compounds shows, in agreement with theoretical results, that the methoxy derivative presents a red-shifted absorption, a higher molecular absorption coefficient and leads to a material of smaller band gap. The evaluation of the photovoltaic properties of the two compounds as donor material in BHJ cells shows that in spite of less favorable optical properties, the biphenyl derivative leads to better performances due to the conjunction of a higher open-circuit voltage and better charge transport properties. Evaluated in simple air processed devices, these preliminary results pave the way to further optimization and device engineering to reveal the true potential of these accessible and greener materials.

4. Acknowledgment

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