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Dendritic-like Molecules Built on a Pillar[5]arene Core as Hole Transporting Materials for Perovskite Solar Cells

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In memory of Prof. François Diederich

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Supporting information for this article is given via a link at the end of the document.

Abstract: Multi-branched molecules have recently demonstrated interesting behaviour as charge-transporting materials within the fields of perovskite solar cells (PSCs). For this reason, extended triarylamine dendrons have been grafted onto a pillar[5]arene core to generate dendrimer-like compounds which have been used as hole-transporting materials (HTMs) for PSCs. The performances of the solar cells containing these novel compounds have been extensively investigated. Interestingly, a positive dendritic effect has been evidenced as the hole transporting properties are improved when going from the first to the second-generation compound. The stability of the devices based on the best performing pillar[5]arene material has been also evaluated in a high-throughput ageing setup for 500 h at high temperature. When compared to reference devices prepared

from spiro-OMeTAD, the behaviour is similar. An analysis of the economic advantages arising from the use of the pillar[5]arene-based material revealed however that our pillar[5]arene-based material is cheaper than the reference.

Introduction

Owing to their high number of peripheral subunits, dendrimers have been intensively used to generate multifunctional nanomaterials with specific properties.^[1] Typical examples are light harvesting molecular devices mimicking the natural

photosynthetic system,^[2] liquid crystalline dendrimers with unusual self-assembly properties,^[3] globular polycationic systems for gene delivery,^[4] and multivalent glycoclusters for biological applications.^[5] The preparation of dendritic structures is however often associated with a large number of synthetic steps thus limiting their applicability. More recently, another concept emerged for the fast preparation of dendritic-like molecules. It relies on the peripheral functionalization of compact molecular scaffolds such as fullerene hexa-adducts,^[6] silsesquioxanes,^[7] or pillar[5]arenes.^[8] In this particular case, the grafting of small dendrons onto the multifunctional core unit already generates globular structures even for low generation numbers.^[9] Owing to the versatile chemistry developed for the functionalization of such molecular scaffolds,^[10] a plethora of nanomaterials became easily available for various applications at the interface of chemistry with physics and biology.^[11-15] For example, fullerene hexa-adducts decorated with boron-dipyrromethene (bodipy) dyes have been used as solar energy concentrators to improve the light-toelectricity conversion of amorphous silicon photocells.^[15] Multibranched three-dimensional hole-transporting materials (HTMs) have been also prepared by grafting extended triarylamine (TAA) residues onto a fullerene hexa-adduct core.^[16-17] These compounds showed interesting features as HTMs in perovskite solar cells (PSCs).^[16] In addition to high photochemical stability. an increased number of peripheral TAA units appeared beneficial to the performances of the photocells.[16,19-21] As part of this research, we became interested in using a pillar[5]arene^[22-23] core to generate dendrimer-like structures with peripheral extended TAA subunits and further investigate the potential of multimeric systems as HTMs in PSCs. Compounds PA02 and PA03 are depicted in Figure 1. When compared to their fullerene-based analogues, pillar[5]arene scaffolds are by far less expensive to

produce which is a clear advantage for future applications. Moreover, the pillar[5]arene core is totally transparent in the visible region and thus parasitic light absorption by the HTM layer should be totally prevented in the PSCs.

Results and Discussion

Synthesis. The synthesis of pillar[5]arene derivatives PA02 and PA03 is shown in Scheme 1. Their preparation is based on the post-functionalization of pillar[5]arene PA01^[8,24] with TAA building blocks under copper-catalyzed alkyne-azide cycloaddition (CuAAC) conditions. The TAA derivatives bearing a terminal alkyne group were prepared from TAA1 by adapting reported procedures.^[25] Sonogashira coupling between TAA1 and triethylsilylacetylene followed by treatment of the resulting TAA2 with tetra-*n*-butylammonium fluoride (TBAF) in CH₂Cl₂ provided clickable building block TAA3. The corresponding extended derivative (TAA5) was also prepared from TAA1. A Buchwald-Hartwig reaction between 4-[(trimethylsilyl)ethynyl]aniline and TAA1 gave TAA4 in a moderate yield (44%). Finally, treatment with TBAF provided terminal alkyne TAA5 in 90% yield. Compounds PA02 and PA03 were then obtained through a 10fold CuAAC reaction between decaazide PA01 and the appropriate TAA precursor (TAA5 and TAA3, respectively). Specifically, the classical CuAAC reaction conditions developed by Sharpless (CuSO₄·5H₂O, sodium ascorbate, CH₂Cl₂/H₂O)^[26] were used to prepare PA02 and PA03. Purification by flash column chromatography followed by recrystallization gave PA02 and PA03 in 55 and 50% yield, respectively.



Figure 1. Structure of the dendrimer-like pillar[5]arene derivatives PA02 and PA03.

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Their structure was confirmed by IR, ¹H and ¹³C NMR spectroscopies and MALDI-TOF mass spectrometry (Figures S1-3). The NMR spectra of PA02 and PA03 were in full agreement with their D₅-symmetrical structure. In both cases, all the peripheral substituents are equivalent and gave rise to a single set of signals. The characteristic features of the pillar[5]arene core were also clearly observed. In the ¹H NMR spectra, a singlet is seen in the aromatic region for the ten equivalent aromatic protons of the pillar[5]arene moiety (δ = 6.45 ppm for **PA02** and 6.52 ppm for PA03). The structure of both compounds was further confirmed by MALDI-TOF mass spectrometry showing the expected molecular ion peak at m/z = 8539.6 for PA02 and 4595.6 for PA03. Importantly, mass spectrometry also provided good evidence for the monodispersity of both compounds. Indeed, no signals corresponding to defected by-products resulting from the incomplete functionalization of PA01 could be observed. The absence of unreacted azide residues was further confirmed by the IR spectra recorded for PA02 and PA03. Effectively, the diagnostic signature of azide units observed at 2085 cm⁻¹ for starting material PA01 could not be detected anymore in the case of PA02 and PA03 (Figure S2).



Scheme 1. Preparation of compounds PA02 and PA03. Reagents and conditions: (a) Triethylsilylacetylene, Pd(PPh₃)₂Cl₂, Cul, PPh₃, piperidine, PhMe, 90°C (76%); (b) TBAF, CH₂Cl₂ (90%); (c) 4-[(trimethylsilyl)ethynyl]aniline, Pd₂(dba)₃, P(*t*Bu)₃, tBuONa, PhMe, Δ (44%); (d) TBAF, CH₂Cl₂ (90%); (e) TAA5, CuSO₄ · 5H₂O, sodium ascorbate, CH₂Cl₂:H₂O (2:1), rt (55%); (f) TAA3, CuSO₄ · 5H₂O, sodium ascorbate, CH₂Cl₂:H₂O (2:1), rt (50%).

Electronic properties. The UV-Vis spectra of both compounds recorded in CH_2Cl_2 (Figure 2a) confirmed that they do not significantly absorb light in the visible region, indicating that the molecules would not compete with light harvesting of the perovskite layer in a solar cell. The red-shift observed for compound **PA02** is probably induced by the superior electron-donor ability of the extended triarylamine group bearing two di(anisyl)amino substituents, with the consequence of enhancing the highest occupied molecular orbital (HOMO) and reducing the

band gap. The optical band gaps of the two compounds were estimated through the determination of the onset wavelength of the spectra (Table 1).



Figure 2. (a) UV-vis spectra of **PA02** and **PA03** recorded in CH_2Cl_2 at 25°C. (b) Cyclic voltammograms of **PA02** and **PA03** on a Pt electrode in $CH_2Cl_2 + 0.1$ M [*n*Bu₄N][PF₆] at a scan rate of 250 mVs⁻¹.

Upon excitation at their optical bandgap, **PA02** and **PA03** show no clear signature of exciplexes reflecting the intramolecular donor-acceptor (CT) interactions, and give a single fluorescence peak with small Stokes shift at 475 and 428 nm, respectively (Figure S4). The transient profiles of fluorescence show single exponential decays with negligible peak shifts (Figure S5-8) both in CH₂Cl₂ solutions and in thin films, showing lifetimes of 2.8 (2.2) and 1.8 (1.2) ns, respectively (lower values were observed in thin films). The partial suppression of the degradation reactions in solid state is a good signal for the stability of the compounds.

The electrochemical characterization of **PA02** and **PA03** was carried out by cyclic voltammetry (CV) measurements on a Pt electrode in CH_2Cl_2 solution + 0.1 M [nBu_4N][PF₆]. The ground-state oxidation potentials are reported in Table 1 and typical voltammograms are shown in Figure 2b.

The HOMO energy levels were estimated from the oxidation potentials in solution *vs.* vacuum for both molecules (Table 1). **PA02** showed higher HOMO values than the reference spiro-OMeTAD^[27] (-4.82 eV *vs.* vacuum, voltammograms are shown in Figure S9 and the chemical structure in Figure 3). The lowest unoccupied molecular orbital (LUMO) energy levels were estimated from the difference between the HOMO and the bandgap. These values agree with the spectroscopic analysis, which confirm the higher HOMO energy for compound **PA02**, as

could be expected due to the presence of stronger electrondonating TAA groups. This view was further supported by DFT calculations (see the Supporting Information for details). For their incorporation in PSCs, the HOMO level of HTM materials has to be higher than the valence band energy of the perovskite.^[21] Importantly, this requirement is fully satisfied for both synthesized pillar[5]arene derivatives.

Table 1: Spectroscopic and electrochemical properties of compounds PA02 and PA03						
	Optical Propertie	S	Electrochemical Properties			
нтм	λ _{max} CH ₂ Cl ₂ (nm)	E _{gap} a (eV)	HOMO ^b (eV)	LUMO° (eV)	E _{ox} d (V)	
PA02	344, 309	3.06	-4.70	-1.64	-0.10	
PA03	324, 307	3.31	-5.01	-1.71	0.21	

^a Estimated from the onset wavelength of the UV-Vis spectra; ^b Estimated from the E_{ox} against ferrocene/ ferrocenium couple of the respective redox waves by means of the following equation: HOMO = -4.8-E_{ox} eV; ^c LUMO = HOMO – Bandgap; ^d obtained from CV measurements and referenced internally to ferrocene.



transparent nature in the visible spectrum as well as the appropriate HOMO levels. To evaluate their potential as HTM, the hole mobility was examined by flash-photolysis time resolved microwave conductivity (FP-TRMC) measurements with spiro-OMeTAD as a reference.^[30, 31] Clear and competitive signature of electrical conductivity transients were observed for both **PA02** and **PA03**, relative to spiro-OMeTAD as depicted in Figure 4. The results obtained for spiro-OMeTAD are shown in Figure S11.

Figure 3. Structure of spiro-OMeTAD used as a reference compound in the present study.

Thermal characterization. Both thermogravimetric (TGA, Figure S10a) and differential scanning calorimetry (DSC, Figure S10b) analyses were performed. The decomposition temperature registered for both **PA02** and **PA03** (respectively, 308 and 306°C) is lower than that registered for spiro-OMeTAD, the reference HTM. Nonetheless, they are both far above the operational temperature of PSCs. On the other side, the transition temperature registered through DSC is lower for spiro-OMeTAD, indicating that a change in the physical state may occur earlier for the reference material. The information extrapolated from DSC analysis might be promising for the stability of the solar cells incorporating these materials with respect to the spiro-OMeTAD reference.

Analysis of the Costs. One of the drawbacks of spiro-OMeTAD is its cost. This is mainly due to the cost of the spiro moiety precursor, 2,2',7,7'-Tetrabromo-9,9'-spirobifluorene (155 €/g)^[28] and the low yields of the synthesis.^[29] This implies that the final cost of the reagents required to obtain 1 g of spiro-OMeTAD is 228.99 €. On the contrary, the high overall yields and the cheap starting materials make the synthesis of the pillar[5]arene molecules much more affordable. In fact, the cost of the precursors required for 1 g of **PA02** is calculated to be only 57.40 €. A detailed analysis of the costs can be found in the Supporting Information (Tables S1-S4).

Hole transporting properties. The potential application of PA02 and PA03 as optoelectronic materials is supported by their



Figure 4. Conductivity transients observed in thin solid films of a) **PA02** and b) **PA03** upon exposure at 355 nm, 9×10^{15} photons cm⁻². Red and blue transients are recorded for pristine films and those after iodine doping, respectively.

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The transients indicated 1.5-fold higher photoconductivity in **PA02** than in **PA03** and spiro-OMeTAD. Upon iodine doping, remarkable enhancement of the transient conductivity was seen in both **PA02** and **PA03**, and recorded 2-fold higher than the reference spiro-OMeTAD. The enhancement suggests clearly the major contribution from photo-injected positive holes as charge carriers. The kinetic traces after I₂-doping shows initial pseudo-first order decays for < 1 μ s regime with the recombination rate constants of 4.1 and 2.0 × 10⁶ s⁻¹. This gives the minimum estimates of hole mobility as 4.0 and 2.6 × 10⁻⁴ cm²V⁻¹s⁻¹ for **PA02** and **PA03**, respectively. These potential hole transporting properties of the novel compounds further motivated us to apply them as hole transporting layer in PSCs.

Incorporation into PSCs. PA02 and PA03 were both introduced in n-i-p mesoporous PSCs to evaluate their potential as HTMs. The novel molecules were deposited by spin-coating on top of Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}PbI₃ perovskite in the following architecture: fluorine-doped tin oxide (FTO)-glass/c-TiO₂/mp-TiO₂/perovskite/HTM/Au. Unless otherwise stated, considering the structural similarity to spiro-OMeTAD, PA02 and PA03 were doped with lithium trifluoromethanesulfonate (LiTFSI), 4-tertbutylpyridine (TBP), and Co(III)TFSI (FK 209) in accordance to their number of N-triarvl mojeties (i.e. spiro has 4. PA03 10, and PA02 30). Additional information on the processing of these materials can be found in the Supporting Information.

Optimization of the devices required several steps. The first one involved finding the right thickness for these HTM layers, which were modified by spin-coating different concentrations of the HTMs in chlorobenzene. A wide range of concentrations was covered, finding the best device performance for **PA02** and **PA03** around 0.003 M, with better initial results for **PA02** (Figure S12-S13). Scanning-electron microscopy (SEM) measurements of cells cross-sections revealed the corresponding thickness to each of the solution concentrations used for the deposition (Figure S14). Figure S15a shows the change in performance of the cells with the thickness of **PA02** layer, suggesting 100 nm as the optimum thickness for this configuration.

The level of doping of the HTMs was also investigated for the better-working HTM PA02. By varying the number of equivalents of the dopants in the HTM solution, it was found that our current conditions of 7.5 equivalents (with respect to spiro-OMeTAD) were the best-performing ones (Figure S15b and S16). A summary of the doping used for each case is included in Tables S5 and S6. These results confirmed that the optimal equivalents of dopants are in direct relationship with the number of N-aryl moieties. In this sense, the equivalents used for the less-branched PA03 were only 2.5 times in respect to spiro-OMeTAD. The influence of the use of FK 209 was also studied, finding that avoiding its use gave improved performance of the cells (Figure S15c). Considering that the use of FK 209 was detrimental, it was not used and just the influence of the other additives was investigated. While it is a very widely employed additive, which has shown many advantages for spiro-OMeTAD, we did not find it beneficial for PA02. There could be reasons related to the properties of the HTMs affecting this behaviour, although it would also be possible to implement this additive for PA02 with further optimization in other experimental conditions. In the same line, Figures S15b-c, S16, and S17 show that none of the dopants is essential for the cell to work. While using no dopant at all leads to a non-working device, using each of them separately (i.e. TBP or LiTFSI) yields a working cell, although still presenting performance problems. It also shows that the optimum amount of TBP is half of the equivalents of LiTFSI with respect to the relative amount in spiro-OMeTAD, to which the recipe was adjusted. Figure S18 includes the external quantum efficiency (EQE) measurements for the best-performing devices, showing integrated J_{sc} values comparable to the ones obtained from the *J*-*V* curves.

The results obtained in this optimization suggest that the doping strategy might have to be adapted to each new case depending on the structure of the molecule to be incorporated. The best doping conditions are summarized in Tables S5 and S6. Once selected the best processing conditions, both HTMs were compared to spiro-OMeTAD. As it can be seen in Figure 5a, devices based on **PA03** barely surpassed efficiencies of 10%, in comparison to the reference devices with spiro-OMeTAD with PCE values over 18%. However, when **PA02** was used as HTM, efficiency values around 16% were reproducibly achieved. Figure S19 summarizes the statistic of the performances of **PA02** and **PA03**-containing cells. The PCE statistics are reported in Figure 5



Figure 5. a) Distribution of PCE values in reverse and forward- (for) and reverse-bias (rev) and b) Current density-voltage (*J-V*) curves of PSCs with spiro-OMeTAD, **PA03** and **PA02** as HTMs. Reverse-bias curves are represented as continuous lines and forward-bias curves as dashed lines.

There seems to be also no improvement in hysteresis with the use of **PA02** or **PA03** in comparison to spiro-OMeTAD. Figure 5b shows the current density-voltage (J-V) curves for both reverse and forward scan measurements for the best performing PSCs for each HTM. The photovoltaic (PV) parameters for these devices

are listed in Table 2. The most efficient device containing **PA02** showed a similar short-current density (J_{SC}) to spiro-OMeTAD (20.67 mA cm⁻²), however efficiency loss is due to both opencircuit voltage (V_{OC} , 1.07 V) and fill factor (FF, 74.8%).

Table 2. Photovoltaic (PV) parameters for most efficient PSCs with spiro-OMeTAD, PA03 and PA02 in both scan directions.

нтм	Scan direction	J _{sc} (mA cm ⁻²)	V _{oc} (V)	FF (%)	PCE (%)
spiro-	reverse	20.77	1.13	77.9	18.21
OMeTAD	forward	20.73	1.09	70.4	15.86
D 4 62	reverse	20.51	1.06	47.2	10.24
PA03	forward	20.11	0.99	31.6	6.31
DA02	reverse	20.67	1.07	74.8	16.56
PAUZ	forward	20.63	1.05	64.5	14.01

The lower V_{OC} value for **PA02** might be related to the slight mismatch in the HOMO energy (-4.70 eV) in comparison to **PA03** (-5.01 eV) and spiro-OMeTAD values (-4.82 eV). Meanwhile, the poor performance of cells with **PA03** (up to 10.24%) is due to the low FF values, which might be indicating a poor charge extraction in this interface. These findings might give a hint on the relevance of the arrangement of the hole-transporting moieties in space, where a higher branching degree of the molecules would lead to improved extraction and hole-transport ability. Therefore, the results give relevant information on the guidelines to follow when designing triarylamine-containing HTMs.

Stability measurements. The stability of devices fabricated with the more efficient **PA02** as HTM were compared to the ones with spiro-OMeTAD. A custom-built high-throughput ageing setup was used to measure the stability for 500 h at different temperatures of 4 devices of each type, each of them containing 6 pixels. Stability tests were carried out at 25, 45 and 65 °C for around 160 h at each temperature in N₂ atmosphere and under MPP load conditions. Additionally, *J-V* scans were taken every 2 h in order to study changes in photovoltaic parameters. Pixels showing significantly different performances were removed from the statistical analysis. Also, a UV-filter was applied to avoid damage due to the sensitization of the TiO₂ layer. Therefore, it should be noted that the *J*_{SC} and PCE values shown on the stability are underestimated.

Figure 6a shows the evolution of PCE, *V*_{oc}, *J*_{Sc} and FF at the different temperatures for devices built with both HTMs **PA02** and spiro-OMeTAD. After a quick burn in FF for spiro-OMeTAD at the beginning of the measurement, that is not occurring with **PA02**, both device types were stable at 25 °C. However, at 45 °C the two HTMs behaved quite differently. Devices based on **PA02** presented a strong decrease in FF, while spiro-OMeTAD-containing ones experienced a significant reduction in *V*_{oc} and *J*_{SC}, parameters in which **PA02** was more robust. The devices were not very stable at 45 °C, having decreased in PCE to half of their initial values. This degradation happened to be even more pronounced at 65 °C, after which cells were showing inferior performance. The enhanced decrease in performance at higher temperatures can be observed in Figure 6b, where the difference between *J*-*V* curves measured at the beginning and the end of the

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same temperature gets bigger the more elevated the temperature is. In addition, the hysteresis increased particularly when the devices were being aged at 45 °C, which can be observed comparing J-V curves of spiro-OMeTAD when starting and finishing the measurement at 45 °C. Overall, no difference can be seen in the decrease of PCE for both HTMs at high temperatures, therefore the higher thermal stability of PA02 in the TG and DSC analysis (Figure S10) does not translate into higher stability of devices at high temperature. This suggests that the thermal properties of the HTM might not be that crucial, or at least not the only factor, to further improve the stability of n-i-p devices. We can see, however, clear behaviour differences for the different HTMs at high temperature, where PA02-based devices decrease in FF, while spiro-OMeTAD ones suffer from Voc and Jsc losses. This could then mean that the HTM nature can lead to different degradation process types.

Conclusion

Two novel multi-branched molecules, PA02 and PA03, have been synthesized and characterized. These compounds have been used in perovskite solar cells as hole-transporting materials. The performances of the solar devices containing these novel compounds have been optimized carefully and compared to a reference model compound (spiro-OMeTAD). The optimized pillar[5]arene-containing cells afforded power conversion efficiencies of 16.56% for PA02 and 10.24% for PA03. Since the performances of PA02 are satisfactory enough when compared to the 18.21% obtained with the reference spiro-OMeTAD, this novel HTM has been also investigated in terms of stability under heating conditions, demonstrating to be highly comparable to the reference after 500 h. Furthermore, an analysis of the costs required for the preparation of PA02 with respect to spiro-OMeTAD revealed a relevant economic advantage for the pillar[5]arene-based compound. Our design principle based on the use of easy to functionalize molecular scaffolds is therefore highly attractive for the preparation of new advanced materials. Importantly, the apparent structural complexity of PA02 is not associated to a difficult synthesis. This is a clear advantage for future developments and this strategy will without any doubt provide new generations of materials associating improved hole transporting capabilities and high stability. Our groups are now working in this direction.

Experimental Section

The preparation and the characterization of all the new compounds as well as the experimental details for the mobility measurements and the device fabrication are described in the Supporting Information.

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Figure 6. a) Solar cell parameters PCE, V_{OC} , J_{SC} and FF over ageing time for solar cells with the HTMs **PA02** and Spiro-OMeTAD. Shown is the average of 11 (**PA02**) and 10 (spiro-OMeTAD) solar cells, error bars show the standard deviation. Ageing was performed in nitrogen with a UV-filter under continuous MPP-tracking (MPP tracks not shown). Additionally, *J-V* curves were taken every 2 h with 100 mV s⁻¹. Temperature was actively controlled and raised from 25°C to 45 °C after 160 h of ageing and to 65 °C after 330 h. Stars mark the *J-V* scans shown in Figure b): Current-voltage behaviour of aged solar cells. The figure shows the scans that were taken at the beginning (solid lines) and at the end (lines with dots) of the ageing periods with 25, 45 and 65 °C.

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Multi-branched three-dimensional organic molecules are an appealing class of compounds that can be employed as hole-transporting materials in high-performance perovskite solar cells. In this work, we present two innovative pillar[5]arene-based HTMs decorated with different triphenylamine fragments. Solar cell performances, stability, and production costs have been deeply investigated with respect to the reference compound spiro-OMeTAD.

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