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## A Methoxydiphenylamine-Substituted Carbazole Twin Derivative: An Efficient Hole-Transporting Material for Perovskite Solar Cells\*\*

Paul Gratia, Artiom Magomedov, Tadas Malinauskas, Maryte Daskeviciene, Antonio Abate, Shahzada Ahmad, Michael Grätzel, Vytautas Getautis,\* and Mohammad Khaja Nazeeruddin\*



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**Abstract:** The small-molecule-based hole-transporting material methoxydiphenylamine-substituted carbazole was synthesized and incorporated into a CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite solar cell, which displayed a power conversion efficiency of 16.91 %, the second highest conversion efficiency after that of Spiro-OMeTAD. The investigated hole-transporting material was synthesized in two steps from commercially available and relatively inexpensive starting reagents. Various electro-optical measurements (UV/Vis, IV, thin-film conductivity, hole mobility, DSC, TGA, ionization potential) have been carried out to characterize the new hole-transporting material.

he hybrid organic–inorganic methylammonium lead iodide perovskite has been intensively investigated by Mitzi et al., for semiconductor and opto-electronic applications.<sup>[1]</sup> Due to the absorption properties and very high molar extinction coefficient of methylammonium lead iodide perovskite, Miysaka et al. have used it as a sensitizer in dye-sensitized solar cells in combination with iodine/iodide as liquid electrolyte.<sup>[2]</sup> The perovskite materials are soluble in most polar and protonated solvents and the fabricated perovskite-sensitized solar cells exhibited very low efficiency and instability. To overcome the disadvantage of the solubility of the perovskite absorber layer, a solid-state dye-sensitized solar cell was constructed using Spiro-OMeTAD as a hole conductor<sup>[3]</sup> along with the perovskite.<sup>[4,5]</sup>

However, the synthesis of Spiro-OMeTAD is prohibitively expensive since it includes reaction steps that require low temperature (-78 °C), and sensitive (*n*-butyllithium or Grignard reagents) and aggressive (Br<sub>2</sub>) reagents. In addition, high-purity sublimation-grade Spiro-OMeTAD is required to obtain high-performance devices. Tremendous efforts have

[*]	P. Gratia, Dr. A. Abate, Prof. Dr. M. Grätzel, Prof. Dr. M. K. Nazeeruddin Group for Molecular Engineering of Functional Materials and Laboratory for Photonics and Interfaces École Polytechnique Fédérale de Lausanne 1015 Lausanne (Switzerland) E-mail: mdkhaja.nazeeruddin@epfl.ch
	A. Magomedov, Dr. T. Malinauskas, Dr. M. Daskeviciene, Prof. V. Getautis
	Department of Organic Chemistry, Kaunas University of Technology Radvilenu pl. 19, 50254 Kaunas (Lithuania) E-mail: vytautas.getautis@ktu.lt
	Dr. S. Ahmad Department Abengoa Research, C/Energía Solar n°1, Campus Palmas Altas, 41014 Sevilla (Spain)
	Prof. Dr. M. K. Nazeeruddin Center of Excellence for Advanced Materials Research (CEAMR) King Abdulaziz University, Jeddah (Saudi Arabia)
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been made to develop alternative molecules with similar performance. However, most of these molecules fail to show performance similar to that of Spiro-OMeTAD.<sup>[6-12]</sup> The only hole-transporting material (HTM) without the spiro motif, known to date that demonstrated device efficiencies close to 15% requires custom-made boronic acids as precursors for the final synthesis.<sup>[13]</sup>

Here we report a new hole-transporting twin molecule (V886), based on methoxydiphenylamine-substituted carbazole, with performance very similar to that of Spiro-OMeTAD. Moreover, it does not require an extensive and expensive synthetic procedure. The high solubility of V886 in organic solvents (e.g.  $> 1000 \text{ mgmL}^{-1}$  in chlorobenzene) makes this molecule very appealing for applications with solution processing. Perovskite solar cells employing V886 as a HTM show power conversion efficiency up to 16.91 %, which is to the best of our knowledge, one of the highest reported values for a small-molecule-based HTM. Furthermore, its simple two-step synthesis the ready availability of the starting materials makes this HTM very appealing for commercial prospects of perovskite solar cells.

The synthesis of V886  $(1345.61 \text{ g mol}^{-1})$  involves the click reaction of 1,2-bis(bromomethyl)benzene with 3,6-dibromocarbazole, followed by a palladium-catalyzed C–N cross-coupling reaction with 4,4'-dimethoxydiphenylamine (Scheme 1). More detailed information on the synthesis can be found in the Supporting Information (SI).

The performance of V886 was tested in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>based solar cells using a mesoporous TiO<sub>2</sub> photoanode and an Au cathode following a procedure based on antisolvent engineering developed by Seok et al. (see SI).<sup>[14]</sup> The perovskite device with V886 shows a maximum power conversion efficiency (PCE) of 16.91% under AM 1.5 G illumination, while PCE values exceeding 14% are routinely observed. The measured fill factor was 0.73, the current density ( $J_{sc}$ ) 21.38 mA cm<sup>-2</sup>, and the open-circuit voltage 1.085 V (Figure 1). The best device from the same batch of solar cells, prepared following the same device fabrication procedure but using Spiro-OMeTAD as hole-extracting layer, displayed a PCE of 18.36% as shown in Figure S1 (SI). The cross-section scanning electron micrograph of the best V886 device is shown in Figure 2.



Scheme 1. Synthetic route to the hole-transporting material V886.



**Figure 1.** Current–voltage characteristics of perovskite solar cells using Spiro-OMeTAD (red) and V886 (black) as hole-transporting materials. The power conversion efficiency of the V886 perovskite solar cell is 16.91%, the open-circuit voltage  $V_{oc} = 1.085$  V, fill factor FF = 0.734, and current density  $J_{sc} = 21.38$  mAcm<sup>2</sup>. The power conversion efficiency of the Spiro-OMeTAD perovskite solar cell is 18.36%.



*Figure 2.* Cross-section scanning electron micrograph of the best device containing a 100 nm thick layer of V886 as a hole conductor.

These perovskite solar cells typically exhibit hysteresis in the current–voltage curve, but according to recent work by Unger et al., very slow scans lead to hysteresis-free currentvoltage curves.<sup>[15]</sup> In the same way, the hysteresis of the V886containing perovskite solar cell decreases with decreasing scan rate as shown in Figure S2 (SI). Fast scan rates (>20 mV s<sup>-1</sup>) lead to significant hysteresis, while scans recorded at 20 mV s<sup>-1</sup> and 10 mV s<sup>-1</sup> show only little hysteresis.

Figure 3 shows the difference in absorbance upon chemical oxidation of V886 by the cobalt(III) complex FK209.<sup>[16]</sup> In its pristine form, V886 absorbs only in the UV region below 450 nm, while the chemically oxidized V886 exhibits visible absorption bands at 628 nm and 814 nm, showing the formation of the oxidized species. Since the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite absorption cuts off at 780 nm, the absorption of the oxidized V886 at 823 nm does not compete. Additionally,



*Figure 3.* UV/Vis absorbance spectra of a) a solution of V886 in chlorobenzene, b) V886 chemically oxidized by addition of 10 mol% FK209. Upon chemical oxidation, peaks at 628 nm and 814 nm appear.

the oxidized V886 does not absorb in the infrared part of the spectrum, as shown in Figure S3 (SI), making this hole conductor an interesting option for the semitransparent devices that are part of a hybrid tandem architecture.<sup>[17]</sup> Moreover, solubility tests show the very high solubility of V886 in some organic solvents like THF and chlorobenzene (>1000 mg mL<sup>-1</sup>).

Lateral thin-film conductivity of V886 and Spiro-OMeTAD layers was measured on a spin-coated thin film (chlorobenzene) on OFET substrates (Table 1). In the

Table 1: Comparison of key properties of Spiro-OMeTAD and V886.

Compound	Spiro-OMeTAD	V886
I <sub>p</sub> [eV] <sup>[a]</sup>	5.00	5.04
I cv [eV vs. vacuum]	5.12	5.27
TOF mobility $\mu_0$ [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ] <sup>[b]</sup>	$4 \times 10^{-5}$	$2 \times 10^{-5}$
TOF mobility $\mu$ [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ] <sup>[c]</sup>	$5 \times 10^{-4}$	$6 \times 10^{-4}$
lateral conductivity	$4.7 \times 10^{-4}$	$4.2 \times 10^{-5}$
(10 mol% FK209) [S cm <sup>-1</sup> ]		

[a] lonization potential was measured from films by the photoemission in air method. [b] Mobility value at zero field strength. [c] Mobility value at  $6.4 \times 10^5$  V cm<sup>-1</sup> field strength.

absence of FK209, no Ohmic contact could be observed and the measured currents were very small compared to the currents measured upon addition of FK209. In the case of oxidized V886, Ohmic contacts are formed with gold and the conductivity upon addition of 10 mol% of FK209 is extracted by making a linear fit and using Ohm's law. The conductivity of oxidized V886 was determined to be  $4.2 \times 10^{-5}$  S cm<sup>-1</sup>, indicating that the chemical oxidation of V886 actually results in doping, that is, an increase of carrier concentration and hence conductivity (Figure 4). It is about one order of magnitude lower than the conductivity measured in the doped Spiro-OMeTAD ( $4.7 \times 10^{-4}$  S cm<sup>-1</sup>). However, it is sufficient for good performance in devices with about 100 nm thick HTM films.



*Figure 4.* Conductivity plot of a doped V886 and Spiro-OMeTAD thin film (log scale and linear scale). Ohmic contacts between doped V886/ Spiro-OMeTAD and the gold contacts are formed. The conductivity of Spiro-OMeTAD is  $4.7 \times 10^{-4}$  Scm<sup>-1</sup> and that of V886  $4.2 \times 10^{-5}$  Scm<sup>-1</sup>.

The hole mobility of V886 films (Table 1) was measured by the xerographic time-of-flight method (XTOF). XTOF measurements indicate that the hole-drift mobility of V886 is  $2 \times 10^{-5} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  at weak electric fields and  $6.4 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  at a field strength of  $6.4 \times 10^5 \text{ V cm}^{-1}$ . The mobility values are of the same order of magnitude as the ones for Spiro-OMeTAD measured in this work and reported elsewhere.<sup>[18]</sup>

When one considers the use of an organic material for optoelectronic applications it is important to know its solidstate ionization potential  $(I_p)$ . The solid-state ionization potential of undoped V886 was measured by photoelectron spectroscopy in air (PESA) and compared to the  $I_p$  of V886 in solution, determined by cyclic voltammetry (CV). The difference between the energies measured in the film (5.04 eV) and in the solution (5.27 eV) could be attributed to the different measurement techniques and conditions (solution in CV and solid film in the photoemission method). The CV measurement also reveals that the HTM undergoes a reversible oneelectron oxidation and the second oxidation peak is at 5.43 eV (Figure S4).

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) measurements reveal that V886 films are amorphous and show good thermal stability; the material starts to decompose at temperatures around 390 °C (Figure 5). DSC scans demonstrated that V886 is fully amorphous and shows the glass transition temperature  $T_g$  at 141 °C (Figure 6). It is higher than that of Spiro-OMeTAD (125 °C),<sup>[18]</sup> indicating a more stable amorphous state. Since V886 is fully amorphous, it is legitimate to link the lateral conductivity to the vertical conductivity, which is a more realistic parameter for characterization of a solar cell based on the architecture described here.

In conclusion, we have demonstrated a small-molecule hole conductor (V886) that yields very high current density (>21 mA cm<sup>-2</sup>) and overall efficiency close to 17% in  $CH_3CH_2NH_3PbI_3$ -based solar cells. V886 is less expensive than the spiro hole conductors: it can be synthesized in two



*Figure 5.* Thermogravimetric heating curve of V886 (heating rate  $10^{\circ}$ C min<sup>-1</sup>).



*Figure 6.* Differential scanning calorimetry: first and second heating curves of V886 (heating rate 10°C min<sup>-1</sup>).

steps from commercially available materials, and is thus useful for large-scale production of perovskite solar cells. The good solubility and film-forming properties allows the formation of thicker films of high quality. We strongly believe that V886 can be also an ideal candidate for other optoelectronic applications such as OLEDs and solid-state dyesensitized solar cells.

**Keywords:** carbyazoles · thin-layer conductivity · organic hole transporters · perovskite solar cells · power conversion efficiency

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