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One-Step Facile Synthesis of a Simple Hole Transport Material for Efficient Perovskite Solar Cells

Hu Chen*†, Daniel Bryant‡§, Joel Troughton§, Mindaugas Kirkus†, Marios Neophytou†, Xiaoh Miao†, James R. Durrant‡§, Iain McCulloch†‡

†King Abdullah University of Science and Technology (KAUST), SPERC, Thuwal 23955-6900, Saudi Arabia.
‡Department of Chemistry and Centre for Plastic Electronics, Imperial College London, Exhibition Road, SW7 2AZ, U.K.
§SPECIFIC, College of Engineering, Swansea University, Baglan Bay Innovation and Knowledge Centre, Central Avenue, Baglan, United Kingdom, SA12 7AX.

ABSTRACT: A hole transporting material was designed for use in perovskite solar cells, with a facile one-step synthesis from inexpensive, commercially available reagents. The molecule comprises a central fluorinated phenyl core with pendant aryl amines, namely, 3,6-difluoro-N,N',N″,N‴,N‴,N‴-octakis(4-methoxyphenyl)benzene-1,2,4,5-tetraamine (DFTAB). A power conversion efficiency of up to 10.4% was achieved in a mesoporous perovskite device architecture. The merits of a simple and potentially low cost synthetic route as well as promising performance in perovskite devices, encourages further development of this material class as new low-cost hole transporting materials for the scale up of perovskite solar cells.

Perovskite solar cells have rapidly become candidates for large scale solar deployment, due to their low cost, ease of processing and demonstrated power conversion efficiencies (PCEs) of >20%. Currently the highest performing lab based devices utilise hole transport materials (HTM) within architectures comprising FTO/TiO₂-bl/mp-TiO₂/Perovskite/HTM, where TiO₂-bl is a dense titania blocking layer, mp-TiO₂ is a mesoporous titania scaffold and the HTM is typically 2,2',7,7'-tetraakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD). Spiro-OMeTAD is able to facilitate devices with high PCEs on a lab scale, however its complicated synthesis and multi-step purification makes it inherently expensive and limits the potential of this material in manufacturing scale production. Additionally Spiro-OMeTAD exhibits an absorption band edge at 400 nm, within the optical spectra of organic-inorganic perovskites, reducing device performance in tandem or reverse illuminated device architectures where light must first travel through the HTM before being absorbed by the photoactive layers.

Recently there have been several new classes of HTMs designed as alternatives to spiro-OMeTAD. Most research has focused on HTMs with improved optical and transport properties, however for scalability, criteria such as reducing the synthesis steps, using less expensive pre-cursors and an ability to be produced in larger volumes, is also necessary. Additionally, ionic additives or p-type dopants, such as lithium bis(trifluoromethylsulfonyl)-imide (Li-TFSI), are often required, in order to increase the conductivity. These additives have been shown to negatively impact the device stability, and elimination of this requirement is beneficial.

Herein we report a new, simple, HTM, comprised of a central difluorinated phenyl ring, tetra-substituted with paramethoxydiarylamine groups (DFTAB). Devices fabricated using DFTAB demonstrated a stabilised PCE of >10%, have a higher energy absorption cutoff than devices utilizing the ubiquitous spiro-OMeTAD, and offer the potential to be used without the addition of ionic additives.

Scheme 1. One-step synthetic route for DFTAB

DFTAB, namely 3,6-difluoro-N,N',N″,N‴,N‴,N‴-octakis(4-methoxyphenyl)benzene-1,2,4,5-tetraamine was synthesized as shown in Scheme 1. The fundamental objectives for the synthesis of DFTAB were the following: only one synthetic step from inexpensive commercial precursors would be permitted, no use of noble metal catalysts, the chemistry should be high yielding, easily scaleable, and purification can be readily accomplished without scale-limiting column chromatography. The synthesis was carried out in a one pot reaction where 4, 4′-dimethoxydiphenylamine was firstly deproto- nated by NaH, followed by nucleophilic aromatic substitution of hexafluorobenzene with in-situ generated amide sodium salt. The product can be recrystallized from common solvents with high (72%) yields. Synthetic procedural details and full chemical characterization are provided in the supporting information. Complete structural characterization was accomplished using standard spectroscopic techniques including 1H NMR and 13C NMR.
NMR, $^{13}$C NMR, HRMS and x-ray and are also included in the supporting information.

The thermal properties were investigated by thermogravimetric analysis (TGA) (Figure S2. in the support information) and differential scanning calorimetry (DSC) (Figure S3. in the support information). The onset of mass loss under nitrogen occurred at around 400 °C, evidence of good thermal stability, while the differential scanning calorimetry (DSC) shows sharp melting peaks at 300 °C, with corresponding crystallisation temperatures of 208 °C on cooling, illustrating large supercooling effects, due to suppressed organization.

![Figure S2](image1.png)

**Figure 1.** Spatial structure (a) and a unit cell (b) of DFTAB determined by X-ray crystallography (hydrogen atoms omitted for clarity).

Single crystal x-ray analysis (Figure 1.) was used to evaluate the molecular conformation and intermolecular packing. DFTAB crystallizes in a monoclinic unit cell, with P2/n space group. The arylamine aromatic rings attached to the N atoms twist from each other, with a dihedral angle of 53° to decrease the electronic repulsion, and enhance the structural stability. The arylamine aromatic rings present almost orthogonal to the central F-phenyl ring, with a dihedral angle of 86°. Packing density calculations reveal that DFTAB has a packing density ratio of 0.6850 based on the occupied volume of 1988.76 Å$^3$ and free volume per unit cell of 914.57 Å$^3$.

Intramolecular π-π interactions are not strongly present in the crystal structures, due to the propeller like orientation of the arylamine aromatic rings, and the orthogonal orientation of the central aryl ring. Weak intermolecular interactions between the aryl amine aromatic groups weakly exist, with relatively large π-π distances ranging from 4.58 Å to 5.92 Å. Full structural and packing detail is available in the supporting information.

![Figure S3](image2.png)

**Figure 2.** Minimum energy conformation of DFTAB calculated using Gaussian (B3LYP/6-31G(d)) to visualize the LUMO and HOMO distribution.

To better understand the molecular orbital properties of DFTAB, density functional theory (DFT) calculations were carried out with Gaussian09 suite at the B3LYP/6-31G(d) level of theory. Figure 2. illustrates that the highest occupied molecular orbital (HOMO) of DFTAB is delocalized over the entire backbone, whilst the lowest unoccupied molecular orbital (LUMO) is mainly localized on the central difluorinated phenyl core. Having the HOMO strongly extended to the periphery of the molecule is expected to enhance intermolecular hole hopping process and subsequent mobility.

The absorption spectra of thin films of DFTAB and spiro-OMeTAD are shown in Figure 3., and the corresponding properties listed in Table 1. DFTAB shows a significant blue-shifted onset of absorption and absorption maximum compared to spiro-OMeTAD, with both molecules exhibiting a relatively large bandgap, due to both the twisted conformation, suppressing pi orbital overlap, and the limited number of electrons participating in the conjugated system. The wider bandgap of DFTAB indicates that it would be a more suitable HTM for use in tandem or MeNH$_3$PbI$_3$ perovskite based devices with reverse illumination architecture.

![Figure 3](image3.png)

**Figure 3.** Thin film UV-vis absorption of DFTAB and spiro-OMeTAD.

The ionization potential of DFTAB was measured using Photo-Electron Spectroscopy in Air (PESA) and the data shown in Table 1. The resonantly donating nitrogen of the arylamine group, extends electron density to the central core, while the peripheral rings are also electron rich from the electron donation of the methoxy groups. This contributes to a low ionization potential of DFTAB (5.2 eV). The inductively electron withdrawing effect of the two fluorine groups on the central phenyl core counterbalances the electron rich aryl amine groups.
Table 1. Optical and Electronic Properties of DFTAB

<table>
<thead>
<tr>
<th>HTM</th>
<th>λ_{abs}/nm</th>
<th>E_{opt, gap}</th>
<th>Ionization Potential (eV)</th>
<th>Electron Affinity (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFTAB</td>
<td>287</td>
<td>3.0</td>
<td>5.2</td>
<td>2.2</td>
</tr>
<tr>
<td>Spiro-OMeTAD</td>
<td>387</td>
<td>3.0</td>
<td>5.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

*obtained from the onset value of absorption.

*b measured by Photo-Electron Spectroscopy in Air (PESA) system.

*c calculated from E_{opt, gap} and IP.

Thin film charge carrier mobilities were measured using the space charge limited current (SCLC) model. The fabricated devices with structure ITO/PEDOT:PSS/HTM/MoOx/Ag were tested under similar conditions as the optimized photovoltaic devices (Table 2). Hole mobility values were obtained by using the following equation:

\[ J_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V_r^2}{L^2} e^{-\left(\frac{0.89\beta}{\sqrt{V_r}}\right)} \]

where \( J_{SCLC} \) is the measured current density, \( \varepsilon_0 \) and \( \varepsilon_r \) are the permittivity and material dielectric constant respectively, \( \mu \) the charge carrier mobility, \( L \) is the film thickness and \( \beta \) is the field activation parameter.

Devices showed hole mobility values of \( 2.9 \times 10^{-5} \text{ cm}^2\text{V}^{-1}\text{sec}^{-1} \) (Figure S5, in the support information), a higher value than Spiro-OMeTAD (\( 2.5 \times 10^{-5} \text{ cm}^2\text{V}^{-1}\text{sec}^{-1} \)) measured under the same conditions.

MeNH₃PbI₃ perovskite photovoltaic cells were fabricated with structure: FTO/bl-TiO₂/mesoporous-TiO₂/MeNH₃PbI₃/HTM/Au. Both HTMs were evaluated with and without tert-butylpyridine and bis(trifluoromethane)sulfonimide lithium salt dopant additives (see supporting information). Typical current-voltage curves for optimised photovoltaic devices are shown in Figure 4.

A simple hole transport molecule was designed and synthesized, with only one-step synthesis from inexpensive starting materials. When used as an HTM in MeNH₃PbI₃ perovskite based photovoltaic devices, a stabilised PCE of 10.4% was achieved and devices exhibit low hysteresis effects. Devices were able to achieve a stabilised PCE of 6% without the addition of ionic additives (Figure S4, in the support information), which is a promising result when long term device stability is considered. The low-cost, straightforward synthetic method, makes this class of molecules promising candidates for hole transport materials in the large scale application of perovskite solar cells.

EXPERIMENTAL SECTION
All compounds were characterized by $^1$H NMR, $^{13}$C NMR on a Bruker Avance III Ultrashielded 600 Plus instrument. High-resolution mass spectrometry (HRMS) data was recorded using a Thermo Scientific - LTQ Velos Orbitrap MS in positive atmospheric pressure photoionization (+APPI) mode. UV-Vis spectra were recorded in a Varian Cary 100 spectrophotometer. Thermogravimetric analysis (TGA) was performed under N$_2$ using Bruker TGA-IR TG209F1 with a ramp of 10 °C/min. Differential Scanning Calorimetry (DSC) was run on DSC-204F1-phoenix. X-ray diffraction measurement of DFTAB was collected on a Bruker D8 Venture diffractometer with PHOTON 100 CMOS detector with an microfocus source (Mo Kα radiation, λ = 0.71073 Å). The computing cell refinement and data reduction was processed using APEX2 software. Packing density calculations were from Material Studio software package (Connolly surface). A Keithley 2400 was employed to obtain the J/V characteristics and hole mobility values. The perovskite photovoltaic cells were fabricated with structure: FTO/bl-TiO$_2$/mesoporous-TiO$_2$/MeNH$_3$PbI$_3$/HTM/Au. The details of the device manufacture were listed in the support information.

ASSOCIATED CONTENT

Supporting Information
This material is available free of charge via the Internet at http://pubs.acs.org/ of DFTAB, $^1$H NMR and $^{13}$CNMR of DFTAB, TGA curve of DFTAB, DSC trace of DFTAB, Device fabrication details, Current-Voltage (JV) Measurements, crystallographic table, CIF file of DFTAB (CIF).

AUTHOR INFORMATION

* Email: hu.chen@kaust.edu.sa

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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REFERENCES

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One-Step Synthesis; Inexpensive starting materials; High yield.