Impact of Fluorine atoms on triphenylamine-based dopant free hole selective layer for perovskite solar cells

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For industrial endeavors, perovskite solar cells (PSCs) demand long-term stability and a cost-effective hole-transporting layer (HTL). The PSC stability can be substantially improved by the rational design of dopant-free HTL that possesses inherent electrical merits. Further, through molecular engineering by placing a fluorinated arm on an established triphenylamine core, superior stability can be achieved, while using cost-effective precursors and easy synthesis routes. Here we developed fluorinated triphenylamine-based HTL, and probed it for structural, electro-optical, and demonstrated the practical utility of HTL in PSCs in its pristine form. The designed fluorinated HTL called tri(3-fluoro-4-methoxy-N-(4-methoxyphenyl)aniline) triphenylene (FOMePh), gave higher power conversion efficiency (PCE) of 17.08% which supersede with doped SpiroOMeTAD (16.9%) while consuming 2.3 times lesser materials as of Spiro-OMeTAD for PSCs fabrication. We made the synthetic cost analysis and FOMePh was calculated to be 80.19 €/g which is four-time lower than the cost of Spiro-OMeTAD. To investigate the impact of fluorine atoms, we synthesize molecules without fluorine atoms (OMePh). The FOMePh and OMePh owned hole mobility of 5.9 × 10⁻⁴ and 3.59 × 10⁻⁵ cm² V⁻¹ s⁻¹, which is on par with doped Spiro-OMeTAD. The photovoltaics parameters suggest the performance of OMePh is dropped due to poor film formation ability as compared to FOMePh, and this has a bearing on the performance and reliability of PSCs.

1. Introduction

Perovskite solar cells (PSCs) have received remarkable attention owing to their outstanding power conversion efficiency (PCE) 1-6 which can save solar energy in the chemical bands by different ways such as water splitting with the production of Hydrogen gas (H₂) and molecular oxygen (O₂) as the clean by-product. 7, 8 PSCs are fabricated following mainly two different configurations which rely on whether the hole transport layer (HTL) or electron transport layer (ETL) is deposited on transparent conducting oxide (FTO) respectively. This former is called "inverted architecture" (positive-intrinsic-negative, p-i-n), while the one is termed as "standard architecture" (negative-intrinsic-positive, n-i-p). 9 The effect of HTLS on hole extraction and stability is fundamental.10,12 However, in n-i-p based PSCS HTLS suffer from low electrical conductivity and hole mobility of p-type organic semiconductors, which is being addressed by the use of dopants. One of the most studied HTL is Spiro-OMeTAD in which the poor electrical properties and high cost limit its widespread application.13, 14 Moreover, in the case of Spiro-OMeTAD, it shows absorbance near to 400 nm and competes with the perovskite light absorbance, which can decrease the PCE since in p-i-n based PSCs light passes from the HTL layer first.15 Arguably, doping can increase the charge extraction to get collected at the contact surface of the HTL and perovskite which triggers high fill factors (FF) and open-circuit voltage (Voc). This doping is being employed in the case of SpiroOMeTAD and many other HTLS such as PEDOT: PSS 16, P3HT 17, and PTAA 18 to increase the conductivity and hole mobility by using Li-based dopants such as LiTFSI and 4-tert-butyl pyridine (t-BP) as an additive. Nevertheless, Li-based dopant harms the stability of PSCs due to their high hygroscopic properties.19, 20 To decrease this problem, Hua et al. investigated the influence of fluorine atoms on the hydrophobicity of Li-dopant. The result showed that higher fluorine atoms (from 2 to 10 atoms) improved charge-carrier transfer and photovoltaic performances in PSCs.21 The design and validation of an innovative cost-effective, dopant-free HTL,22 with good electrical properties and high stability are paramount for scalability.23 Fluorinated-based molecular semiconductors have high hydrophobicity, and rational molecular packing to trigger higher hole mobility and conductivity with compatible energy levels to perovskite as HTLS.25 Recently, doped fluorinated Spiro-OMeTAD with PCE of 24.8% is reported. This PCE is correlated to lowering energy levels in fluorinated compared to pristine one and enhancing molecular packing in PSC.6 To fabricate dopant-free PSCs, pyrene-based HTL was synthesized in multi-steps with triphenylamine substituents and device performance was investigated. The result showed fluorinated HTL has a better PCE compared with pristine HTL (5.9% vs 5.0%), and was ascribed to the quality of the film.26 In a similar fashion central fluorinated phenyl core with pendant aryl amines-based PSCs achieved a stabilized PCE of 6% without the addition of ionic additives.27 Hao et al. synthesized a new HTL with benzo di-thiophene core and di-fluorobenzene and 4,4’-di-methoxydiphenylamine as the branches called BDTOFMeDPA. The optimized PSCs with fluorinated HTL afford a decent PCE of 14.5%, while the non-
fluorinated one delivered a PCE of 11.3% under similar conditions. This increase in PCE is related to increasing photocurrent density associated with efficient charge carrier extraction and collection. The authors noted fluorine atoms affected the tuning of energy levels. Besides, high stability and PCE, the cost has a paramount effect on industrialization. Triphenyl amine (TPA) based HTLs are one of the most cost-effective materials. Bonaccorso et al. reported TPA-based HTLs with phenyl-4-(phenyldiazenyl) aniline branches, of which 1 g of this new HTL (TPA-AZO) costs $22.76 which is remarkably lower compared to that of Spiro-OMeTAD ($170–475). However, dopant-free TPA-AZO only showed 10.07% PCE. In the same direction, TPA core and diphenylethenyl sidearms were synthesized which only showed 10.79% with comparable FF and Voc. While the reported structure without dopants or additives, a dopant-free HTL based on 2,2’-bithiophene is reported for an p-i-n devices. Herein, we have designed and synthesized fluorinated TPA-based HTL (FOMePh) from inexpensive precursors to investigate the effect of fluorine atoms on the film-formation, optoelectrical properties of HTL, performance, and stability of dopant-free HTL based PSCs. The FOMePh HTL in pristine state yielded an outstanding photovoltaic performance as compared to common doped Spiro-OMeTAD because of molecular packing and high-quality film formation ability. While the reported structure without fluorinated atoms (OMEPh) showed an inferior behavior due to poor film-forming ability and non-aligned energy level. Undoped FOMePh showed on par performance and comparable FF and Voc to the doped Spiro-OMeTAD (17.08 % vs 16.90 %). The molecular structures of HTLs employed in the present work are shown (Scheme 1).

![Molecular structures of the designed HTLs](image)

**Scheme 1. Molecular structures of the designed HTLs**

2. Experimental

2.1. Materials

Materials for synthesis: All the compounds include bromine (Br₂), 3-fluoro-4-methoxy-N-(4-methoxyphenyl)aniline, bis(4-methoxyphenyl)amine, palladium(II) acetate, sodium tert-butoxide, MgSO₄, Tri-tert-butylphosphine, were purchased from Fisher Scientific and TCI. Spiro-OMeTAD was purchased from Sigma Aldrich. Solvents were purchased from local distributors and were used without further purification. All the reactions were carried out under an inert environment in a Schlenk tube under N₂. Materials for Device Fabrication: Lead Iodide (99.9%) and formamidinium iodide (FAI) were purchased from Tokyo Chemical Industry (TCI) and employed as received. Lead bromide, LiTFSI, tert-butyl pyridine (TBP) were purchased from Sigma-Aldrich. Common solvents such as DMF, DMSO, isopropanol, ethanol, chlorobenzene were purchased from Acros Chemicals and used as received.

2.2. Instrumentation

**1H and 13C NMR spectra were recorded with a Varian Mercury 500 MHz spectrometer in C₂D₂ solvent. The differential scanning calorimetry (DSC) signals were recorded using a Mettler Toledo DSC 1 apparatus. ESI-Mass experiments were performed using a micro mass Q-TOF mass spectrometer. UV/Vis spectroscopy was performed using a Cary 60 (Varian) UV/Vis spectrophotometer.**

2.3. Device Fabrication

**n-i-p: Fluorine doped tin oxide (FTO) coated glass (NSG 11) and was cleaned in a sequence before use. Ultrasonication (2% Hellmanex water solution for 30 minutes) followed by rinsing with deionized water, acetone, and then isopropanol (IPA) was used and lastly, the electrodes were treated under UV-Ozone for 30 minutes for the removal of any residue on the surface. TiO₂ compact layer was deposited on the cleaned FTO substrate via spray pyrolysis at 450 °C using a precursor solution of titanium disopropoxide bis(acetylacetonate) in anhydrous ethanol (1:19). The substrates were left at 500 °C for a further 30 minutes post spray and then left to cool down. The mesoporous TiO₂ layer was deposited on these electrodes through spin coating process (30 s at 4000 rpm), for this, a TiO₂ paste (Dyesol 30 NR-D) was diluted to 1:8 in ethanol. The substrates were annealed first at 125 °C, followed by 500 °C in four-step heating, and were finally also maintained at 500 °C for 30 min. On attaining room temperature, the substrates were treated under UV-Ozone for 15 minutes and transferred to an argon-filled glove-box for perovskite layer deposition. The precursor solution for preparing the mixed perovskite (FAPbI₃)₀.₈₅(MAPbBr₀.₁₅) was prepared by dissolving FAI (1 M), PbI₂ (1.2 M), MABr (0.2 M), and PbBr₂ (0.2 M) in anhydrous DMF; DMSO 4:1 (v/v). The perovskite solution was spin-coated in a two-step sequence at 1000 and 6000 rpm for 10 and 30 s, respectively. During the second step, 110 µL of chlorobenzene was dripped as an antisolvent approach on the substrate 10s before the end of the spinning process. The perovskite-coated substrates were annealed at 100 °C for 1 h in a glovebox. On acquiring room temperature, the hole selective layer was deposited. Spiro-OMeTAD (70 mM) was prepared by dissolving the corresponding amount of materials in 1 mL chlorobenzene. Spiro-OMeTAD was doped by adding bis-
(trifluoromethylsulfonyl) imide lithium salt (Li-TFSI) and 4-tert-Butylpyridine (t-BP) in the molar ratio 0.5 and 3.3 respectively. 40 μL of HTL solutions were spin-coated atop of the perovskite layer at 4000 rpm for 30 s, in an argon-filled glove box. Similarly, 30mM each of FOMePh and OMePh were pre-heated at 85°C and 75°C respectively and deposited atop the perovskite layer. The device fabrication was finished by evaporating a thin silver layer of 100 nm as a cathode under a low vacuum (10⁻³ torr). All solutions were prepared inside an argon-filled glove box with controlled moisture and oxygen conditions (O₂ <15 ppm, H₂O < 2 ppm).

3. Results and discussion

3.1 Characterization of new HTLs

FOMePh is reported here for the first time (Scheme 2) with a good yield while OMePh was synthesized according to the last report with modification.34,35 Scheme 2 represents, a one-pot method used for coupling between the main core, which is tris(4-bromophenyl)amine (similar to the previous report)35 and the branches, which are 2-fluoro-4-methoxy-N-(4-methoxyphenyl)aniline. The final compounds were characterized by an array of spectroscopic techniques such as NMR (Figure S1 and S2), mass spectroscopic (Figure S3), UV-vis (Figure 1A and S4A) Cyclic voltammetry (CV) (Figure 1B and S4B), and DSC (Figure 1C).

![Scheme 2. Reaction scheme for the synthesis of the FOMePh.](image)

The UV-vis absorption spectra of OMePh and FOMePh in solution dissolved in dichloromethane solvent and a thin film deposited on glass substrate were measured (Figure 1A and Figure 4A) and are tabulated in Table 1. OMePh and FOMePh display three absorption bands at 300-350 nm and 400-450 nm regions. The two absorption bands in the 300-320 nm region can be assigned to the π-π* transition of the TFA moieties, while the absorption in 400-450 nm is assigned to the intramolecular charge transfer of π-τ* electronic transition.36 OMePh shows a λ_max at 346 nm, while FOMePh shows 337 nm. We ascribed this trivial blue shift to the decreased electron-donating ability of the fluorinated TPA unit in FOMePh due to the presence of electron-negative fluorine atoms. Furthermore, we noted in thin-film (Figure S4), the UV–vis spectra show slight red-shifting due to molecular π–π* stacking.37,38 We derived the HOMO and LUMO energy levels with the help of cyclic voltammetry. Due to the presence of fluorine atoms in FOMePh, we can deduce a shift of 51 mV in the redox wave for OMePh (Figure 1B). The electrochemical properties of the new HTLs show three consecutive reversible redox peaks which confirm the stability of HTL in solution media. To calculate the HOMO energy levels, the onset oxidation potentials (vs Ag/Ag⁺) corresponding to OMePh and FOMePh were calculated to equal to -0.16 and -0.10 V. Applying E_{ox,onset} in E_{HOMO} (eV) = - (E_{ox,onset} - E_{ferrocene,onset} + 5.1), where E_{ferrocene,onset} is 0.11 V, the resulted HOMO levels are -4.89 eV and -4.83 eV respectively for FOMePh and OMePh. Here the effect of fluorine atoms on HOMO level decrement is visible39 arguably, this will allow achieving higher V_OC in devices. The optical band gaps were used to calculate the LUMO levels of new HTLs, E_{LUMO} = E_{HOMO} + E_{gap}, and the values calculated -2.1 and -1.9 eV, respectively for OMePh and FOMePh (Table 1).

| HTL         | λ_max (nm) | λ_onset (nm) | E_{opt} (eV) | E_{HOMO} (eV) | E_{LUMO} (eV) | Tg (°C) | cond. (μS cm⁻¹) | Mobility (× 10⁻⁴ cm² V⁻¹ s⁻¹) |
|-------------|------------|--------------|--------------|---------------|---------------|---------|----------------|-------------------------------|
| FOMePh      | 337        | 408          | 3.0          | -4.9          | -1.9          | 105.7   | 36.2           | 5.9                           |
| OMePh       | 346        | 454          | 2.7          | -4.8          | -2.1          | -        | 12.0           | 0.4                           |
| Spiro-OMeTAD (doped) | 383        | 425          | 2.9          | -5.1          | -2.2          | 124.4   | 36.0           | 6.3                           |

To evaluate the thermal stability, differential scanning calorimetry (DSC) measurements were made. The second cycle DSC curves are shown (Figure 1C) for OMePh and FOMePh. FOMePh shows a T_g at 105.7°C, however, no sign of glass transition temperature (T_g) was observed for OMePh. The descent thermal stability of FOMePh will ensure PSCs operation in extreme conditions (> 85 °C).

To gaze at the impact of molecule engineering on electrical properties, we measured conductivity and hole mobility.40 The conductivities of pristine FOMePh and OMePh were derived by measuring the linear current-voltage curves of the device (FTO/HTL/Ag). The conductivities of FOMePh, OMePh were 36.2 and 12 μS cm⁻¹, respectively (Figure 1D), which is on par with the conventional doped Spiro-OMeTAD (36 μS cm⁻¹).

The hole mobilities of pristine FOMePh, OMePh along with the doped Spiro-OMeTAD were derived by fitting the J_0.5-V curves obtained from hole-only devices (FTO/PEDOT:
PSS/HTL/Ag, the HTL film thickness is 120, 76, and 33 nm for Spiro-OMeTAD, FOMePh, and OMePh respectively (Figure S5). The hole mobility of pristine FOMePh, OMePh, and Spiro-OMeTAD was calculated as $5.9 \times 10^{-4}$, $3.59 \times 10^{-5}$ and $6.3 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ respectively. Pristine FOMePh exhibits higher hole mobility than other fluorinated HTLs$^{41}$ and comparable hole mobility value as of doped Spiro-OMeTAD, suggesting its potential as dopant-free HTL for PSCs (Figure 1E).

To examine the microstructure of perovskite and different HTL coated perovskite, we performed scanning electron microscope (SEM) and atomic force microscopy (AFM) measurements. It is obvious from the SEM image that the perovskite layer exhibits a pinhole-free, compact, and uniform surface morphology (Figure 2A). The microstructure of the FOMePh and OMePh (Figure 2B and 2C) layers reveals homogenous and heterogeneous surfaces respectively. OMePh shows a rough surface together with a slow crystallization as microwires. We suggest the fluorine atoms have a predominant influence on the film-forming abilities while OMePh shows crystallization over the perovskite surface in chlorobenzene solvent. The surface topography deduces from AFM images, display the perovskite film exhibits the maximum surface roughness (RMS) of 21.7 nm (Figure S6). After coating with different HTLs, the roughness decreases significantly. The RMS value decreases in the order of OMePh (8.34 nm) > Spiro-OMeTAD (4.65nm) > FOMePh (4.23 nm). The top-view microstructure of the FOMePh and Spriro-OMeTAD indicates that FOMePh and Spiro-OMeTAD lead to uniform and full coverage of HTL on perovskite. While in the case of OMePh the surface roughness increases, ascribed to the formation of intermittent and incomplete coverage on the perovskite film.

To elucidate the interaction between FAMA and FOMePh, the elemental composition on the surface of pristine perovskite and coated by FOMePh is investigated by X-ray photoelectron spectroscopy (XPS) spectra. The core-level peaks of C, N, F and Pb elements are shown in Figure 3. The component at 283.7, 285.2, and 287.2 eV in C1s spectrum are related to C-C of C=NH$^+$, and C-NH$^2$+ in FA respectively (Figure 3A),$^{43, 44}$ Difference in the intensity of C-NH$^+$ and C=NH$^2$+ peaks are in line with the ratio of FA and MA in FAMA. In the FAMA sample coated with FOMePh, the intensity of C-C and C-N has been decreased and shifted 0.9 and 0.7 eV toward higher binding energy respectively (Figure 3B). While the component in N1s spectra at 399.4 and 401.0 eV are related to C=NH$^+$ and C-NH$^2$+ respectively, the new shoulder at 400.6 eV is related to N in Spiro-OMeTAD (blue), FAMA_FOMePh (green), FAMA-spiroOMeTAD (purple), and FAMA_OMePh (green). The peak represented by * is from FTO.

To elucidate the interaction between FAMA and OMePh, the elemental composition on the surface of pristine perovskite and coated by FOMePh is investigated by X-ray photoelectron spectroscopy (XPS) spectra. The core-level peaks of C, N, F and Pb elements are shown in Figure 3. The component at 283.7, 285.2, and 287.2 eV in C1s spectrum are related to C-C of C=NH$^+$, and C-NH$^2$+ in FA respectively (Figure 3A),$^{43, 44}$ Difference in the intensity of C-NH$^+$ and C=NH$^2$+ peaks are in line with the ratio of FA and MA in FAMA. In the FAMA sample coated with FOMePh, the intensity of C-C and C-N has been decreased and shifted 0.9 and 0.7 eV toward higher binding energy respectively (Figure 3B). While the component in N1s spectra at 399.4 and 401.0 eV are related to C=NH$^+$ and C-NH$^2$+ respectively, the new shoulder at 400.6 eV is related to N in Spiro-OMeTAD (blue), FAMA_FOMePh (green), FAMA-spiroOMeTAD (purple), and FAMA_OMePh (green). The peak represented by * is from FTO.

Figure 1. (A) UV-vis absorption spectra of FOMePh and OMePh in dichloromethane (DCM) solvent (20 μM). (B) CV of 1mM FOMePh and OMePh in 0.1 M nBu$_4$NPF$_6$ in DCM. (C) DSC curves of FOMePh and OMePh (D) I−V curves measurements to derive the conductivity of different HTLs (device structure: FTO/HTL/Ag) of the HTLs and (E) J−V characteristics of devices measured to calculate the hole mobility of different HTLs.

Figure 2. Top view of SEM (A) Mixed perovskite (FAMA), (B) FOMePh, (C) OMePh with a scale bar of 1 μm. The inset in B and C represents the image for film formation on the device surface, D) XRD patterns of pure FAMA perovskite (red), FAMA- Spiro-OMeTAD (blue), FAMA-FOMePh (purple), and FAMA-OMePh (green). The peak represented by * is from FTO.

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| 4 | J. Name., 2012, 00, 1-3 | This journal is © The Royal Society of Chemistry 20xx |
O1s of the FOMePh which does not exist in FAMA (Figure 3D and E). The core-level spectrum of lead (Pb2+) presents two distinct peaks at 137.2 and 142.1 eV. On HTL deposition, these peaks shifted (0.51 and 0.48 eV), suggesting an interaction between N atoms in FOMePh and Pb2+ (Figure 3F).

Figure 3) X-ray photoelectron spectroscopy (XPS) spectra of C1s (A) for pristine FAMA and (B) for FAMA coated with FOMePh, (C), N1s, (D) F1s, (E) O1s, and (F) Pb4f for FAMA and FAMA with FOMePh.

3.2 Photovoltaic Performance

To investigate the hole transport properties of synthesized HTL, we fabricated n-i-p type PSCs having the structure, FTO/bl-TiO2/mp-TiO2/FAMA/FOMePh or OMePh/Au. While doped Spiro-OMeTAD was used as an HTL for the control PSCs. The energy level diagram and device configuration are presented (Figure 4A and 4B). The scanning electron microscopy (SEM) image of the cross-sectional PSC (Figure 4C), depict layers structure, with FOMePh is represented.

![Figure 4](image)

Figure 4. (A) Energy level diagram, (B) device configuration of fabricated perovskite solar cells using (FAPbI3)$_x$(MAPbBr$_3$)$_{1-x}$ perovskite as an absorber, and (c) typical cross-sectional SEM image of PSC with FOMePh.

The average and champion PSC performance parameters are listed (Table 2). We noted that the pristine fluorinated HTL shows a highly competitive performance with a champion PCE of 17.08% using only 30 mM of the FOMePh, a PCE of 16.9% was recorded for the PSCs with 70 mM of doped Spiro-OMeTAD. The impact of fluorine atoms on the performance of the PSC was prominent when compared with OMePh, which gave a mere PCE of 4.93%. Device statistics and optimized concentration of FOMePh for device fabrication are presented in Figure S7 and Table S1 respectively.

![Table 2](image)

| HTL              | $V_{oc}$ (mV) | $J_{sc}$ (mAcm$^{-2}$) | FF (%) | PCE (%) (average) | HI |
|------------------|---------------|------------------------|--------|-------------------|----|
| FOMePh (Pristine)| 980.14        | 23.95                  | 72.53  | (15.3±0.8)        | 0.04 |
| OMePh (pristine) | 836.60        | 19.05                  | 30.95  | (3.96±0.8)        | 0.15 |
| Spiro-OMeTAD     | 1048.09       | 21.94                  | 73.51  | (15.6±1.0)        | 0.06 |

We noted that in the past reports dealing with the addition of fluorine atoms in HTLs resulted in a 5.2, 0.9% or 0.04% increase in PCE. The high fill factor (FF) and open-circuit voltage ($V_{oc}$) with the use of FOMePh as HTL, suggests the decisive role played by the fluorine atoms favors improved microstructure on top of the perovskite layer, further from microscopy images we deduced uniform and full coverage on perovskite. This promotes an efficient charge extraction at the interface between perovskite and FOMePh$^*$ (Table 2, Figure 5A).

The hysteresis index (HI) is calculated for the forward and reverse scan directions showing low HI of both Spiro-OMeTAD and FOMePh (Table 2, Figure S8). The external quantum efficiency (EQE) covers the range from 300 – 900 nm explaining a high photon to electron conversion and reaching a maximum of ~87% in the case of Spiro-OMeTAD and FOMePh while for OMePh, it reached a maximum up to 73% (Figure S5B). The integrated $J_{sc}$ values from the IPCE spectra are 19.75 and 19.65 mAcm$^{-2}$ for the FOMePh and Spiro-OMeTAD respectively which are in line with $J_{sc}$ obtained from $J$-$V$ measurements. The steady-state photocurrent density measurements are done under AM 1.5G 100 mW/cm$^2$ continuous illumination in ambient conditions for 300s. Figure 5C shows the evolution of the photocurrent density for ~300s is completely stable.

3.3 Device kinetics

To investigate the charge extraction behavior at the FAMA/HTM interface, the steady-state photoluminescence (PL) spectra of the perovskite were recorded on the quartz substrate and excited at 500 nm (Figure 5D). The pristine perovskite emits an emission peak at 764 nm. In the case of FAMA/FOMePh, the reduction in the PL intensity indicating the fluorinated HTM (FOMePh) assists photo-generated holes extraction from the perovskite to the hole transporting layer. The result shows the charge carrier extractions at interfaces are enhanced by the FOMePh due to higher PL quenching compared with Spiro-OMeTAD.

Table 2. Photovoltaic parameters derived from $J$-$V$ measurements of n-i-p devices.
To further clarify the improvement in PV parameter, Mott–Schottky and impedance analysis of devices based on different HTL was conducted. Mott–Schottky measurements were done at 10 kHz under dark conditions. From the X-intercept of the linear regime in the Mott–Schottky plot (Figure S10), the built-in potential can be derived. The built-in potential ($V_b$) of the PSC based on FOMePh (990 mV) is marginally higher than that of the PSC based on OMePh (980 mV).

The charge transfer dynamics and recombination mechanism in PSCs with dopant-free FOMePh and doped Spiro-OMeTAD were elucidated by electrochemical impedance spectroscopy (EIS) under dark conditions. To analyze the EIS data, the device was modeled using an equivalent circuit model of $R_{s}+R_{ct}/CPE1+R_{rec}/CPE2$ (Figure S11), where $R_{s}$, $R_{ct}$, and $R_{rec}$ represent series resistance, charge transfer resistance at the interface of Au/HTL/perovskite, and recombination resistance respectively (Table S2).40,45,46 and the fitted Nyquist plot and bode plots are shown in Figure 6A and B at 0.95 V applied bias voltage. We noted that at a given bias, the $R_{ct}$ in the device with thin HTL of FOMePh is much lower than that of the reference device with doped Spiro-OMeTAD, deducing that the HTL imparts a significant role in promoting the charge transfer dynamics at the perovskite/HTM/Au interface (Figure 6C).

Further, the $R_{rec}$ values (in Figure 6D) are higher for the PSCs with FOMePh than that of the Spiro-OMeTAD-based PSCs, suggesting less charge recombination loss between the perovskite film and FOMePh layer (Table S2). The ideality factor ($n$) was derived from the relation$^{37}$ followed by $R_{rec}=Ae^{\beta(V_{app}/K_{B}T)}$ and $n=1/\beta$. The obtained $\beta$ values for the devices with FOMePh and Spiro-OMeTAD were 0.48 and 0.52, respectively, corresponding to the $n$ values of 2.08 and 1.92.

To elucidate the impact of different HTMs on charge lifetime ($\tau$), Bode phase spectra were conducted under dark conditions at 0.95 V (Figure 6C). The charge lifetime can be derived using $\tau = 1/(2\pi f_p)$, where $f_p$ denotes the peak frequency corresponding to the charge-transfer process at perovskite/HTM interface.$^{48}$ The FOMePh-based PSC showed a longer charge lifetime of 5.20 μs compared to that in the reference PSC with doped Spiro-OMeTAD (3.18 μs). The longer charge lifetime can be ascribed to the lessened charge recombination at the interface of perovskite/FOMePh, resulting in rapid charge carrier transport of the PSC with FOMePh, which is in agreement with the upgraded $J_{sc}$ obtained from the J-V curve. The origin of different carrier recombination kinetics in FMeOPh, OMePh, and SpiroOMeTAD based PSCs is further investigated by dark current measurement$^{45}$ (Figure S9).

$$J_{dark} = J_0 \left[ \exp \left( \frac{V}{nqV_{app}K_{B}T} \right) - 1 \right]$$

Ideality factor ($n_{ide}$) and saturation current ($J_0$) are calculated by fitting the data to the above Equation, where $J_{dark}$ is the dark current density, $V$ is the applied voltage, $q$ is the electron charge, $K_B$ is the Boltzmann constant, $T$ is the temperature. In the semi-logarithmic J-V curve, the dark reverse saturation current (under negative bias) in the FMeOPh is lower than that of the OMePh, leading to higher $J_{sc}$. Compared with OMePh ($J_0$=780 μA/cm$^2$), FOMePh and Spiro-OMeTAD showed lower leakage current of 0.18 μA/cm$^2$ and 0.0031 μA/cm$^2$ respectively. The ideality factor of 2.01, 2.17, and 2.57 were calculated from the slope in the forward direction for Spiro-OMeTAD, FOMePh, and OMePh respectively. The smaller values of the $n$ and $J_0$ for FOMePh and Spiro-OMeTAD based PSCs imply reduced interfacial recombination, and consequently, charge transportation and thus PV performance are improved.
3.4 Device stability and cost calculation
For reliability, long-term device performance is an important characteristic for the operation of PSCs. In the case of n-i-p device configuration (present case), hydrophobic HTL deposited on top of perovskite has two-fold functions. The HTL extracts and transports holes and also serves as protecting barrier towards atmospheric moisture. Thus, to investigate surface hydrophobicity, water contact angle measurement was performed. FOMePh shows a higher water contact angle than Spiro-OMeTAD and OMePh indicating its better hydrophobicity due to the strong effect of fluorine atoms on film forming and hydrophobicity in PSCs (Figure 7A-C).

Furthermore, to note the long-term stability of PSCs based on FOMePh, OMePh, Spiro-OMeTAD, MPP tracking of un-encapsulated devices was investigated under continuous 1 sun illumination in ambient condition (~40-50% RH). FOMePh-based PSCs exhibited higher stability compared to that of Spiro-OMeTAD-based PSCs, (Figure 7D) and, 60 % of its initial PCE was retained for ~ 80 hr, while Spiro-OMeTAD retains only 20% of its initial PCE. The improved stability of the FOMePh-based PSCs is ascribed to the combined results of the uniform HTM protecting layer without any external dopants and its superior hydrophobicity. Figure 7E displays the PCE of the devices kept outside of the glove box in dark and under air condition (~20% RH) measured under AM 1.5G voltage deficit. Our future strategies will be focused to tune the HOMO level by adding reliable hole selective layers development. Our future strategies will be focused to tune the HOMO level by adding dopant/additives and supersede in performance (17.08%) as compared to doped Spiro-OMeTAD (16.90%). FOMePh improves film formation, yields competitive hole mobility, and a suitable energetic level in its dopant-free state suggests the impact of fluorine atoms to decrease the interfacial obstacle for hole extraction as shown by steady-state fluorescence quenching and decreases the series resistance, and improve the fill factor.

Finally, for industrial endeavors, the calculated costs show that FOMePh has a significantly lower estimated price (80.19 €/g, Table S3, and S4) compared with the Spiro-OMeTAD and works effectively in its pristine form.

We designed and developed fluorinated triphenyl amine-core-based hole-transporting materials for PSCs. The FOMePh can be synthesized from cost-effective precursors in a single-step reaction, to reduce the cost/watt ratio. Fluorinated-based FOMePh exhibit high hydrophobicity, and higher hole mobility due to molecular packing and aligned energetic levels for perovskite. We also synthesized a similar analog without fluorinated atoms (OMePh) to deduce the impact of fluorine atoms on structural and optoelectrical properties. OMePh showed an inferior behavior due to poor film-forming ability and non-aligned energy level. Due to high charge mobility in pristine form, FOMePh works efficiently using low molar concentration (30mM) without any dopant/additives and supersede in performance (17.08%) as compared to doped Spiro-OMeTAD (16.90%). FOMePh improves film formation, yields competitive hole mobility, and a suitable energetic level in its dopant-free state suggests the impact of fluorine atoms to decrease the interfacial obstacle for hole extraction as shown by steady-state fluorescence quenching and decreases the series resistance, and improve the fill factor.

Conflicts of interest
There are no conflicts to declare.

Acknowledgments
This work has received funding from the European Union H2020 program under the European Research Council Consolidator grant MOLEMAT (726360), and ARISE (PID2019-111774RB-100), from the Spanish Ministry of Science and Innovation and Basque regional ELKARTEK project ENSOL2.

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Figure 7. Hydrophobicity and PSC stability: Water contact angle (A) Spiro-OMeTAD, (B) FOMePh, and (C) OMePh, (D) PCE measured for over 30 days, and (E) maximum power point tracking for the FOMePh and Spiro-OMeTAD based PSCs without encapsulation for ~80 hr under 1 sun illumination at 27°C and 40-50% humidity condition.

Finally, for industrial endeavors, the calculated costs show that FOMePh has a significantly lower estimated price (80.19 €/g, Table S3, and S4) compared with the Spiro-OMeTAD and works effectively in its pristine form.
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