Hole-Transporting Materials for Perovskite Solar Cells Employing an Anthradithiophene Core

José Santos,* Joaquín Calbo, Rafael Sandoval-Torrientes, Inés García-Benito, Hiroyuki Kanda, Iwan Zimmermann, Juan Aragó, Mohammad Khaja Nazeeruddin,* Enrique Ortí,* and Nazario Martin*

ABSTRACT: A decade after the report of the first efficient perovskite-based solar cell, development of novel hole-transporting materials (HTMs) is still one of the main topics in this research field. Two of the main advance vectors of this topic lie in obtaining materials with enhanced hole-extracting capability and in easing their synthetic cost. The use of anthra[1,9-bc:5,10-6′-c′]dithiophene (ADT) as a flat π-conjugated frame for bearing arylamine electroactive moieties allows obtaining two novel highly efficient HTMs from very cheap precursors. The solar cells fabricated making use of the mixed composition (FAPbI )0.85(MAPbBr )0.15 perovskite and the novel ADT-based HTMs show power conversion efficiencies up to 17.6% under 1 sun illumination compared to the 18.1% observed when using the benchmark compound 2,2′,7,7′-tetakis(N,N-di-p-methoxyphenyl-amine)-9,9′-spirobifluorene (spiro-OMeTAD). Detailed density functional theory calculations allow rationalization of the observed opto-electrochemical properties and predict a flat molecular structure with a low reorganization energy that supports the high conductivity measured for the best-performing HTM.

KEYWORDS: anthradithiophene, hole-transporting material, perovskite, solar cells, theoretical calculations

INTRODUCTION

The relevance of the research on perovskites for solar energy conversion can be weighted in terms of the publication volume on the topic. The astonishing number of 15,996 scientific articles referring to “perovskites for photovoltaics” in the 2009–2021 period (more than 3,600 articles in 2019), with Miyasaka’s paper being cited more than 9,800 times,1 perfectly reflects how hot this topic is. The research effort these numbers represent translates into the power conversion efficiency (PCE) leap reported for perovskite-based solar cells from 3.8% in 2009 to the current record of 25.5%.2 Originally consisting of an active layer of the CH3NH3PbI3 hybrid perovskite deposited on top of a layer of mesoporous TiO2, perovskite solar cells (PSCs) have undergone many modifications. Sandwicking the perovskite active layer between an n-type and a p-type semiconducting material, respectively acting as electron- and hole-transporting layers, allowed a major breakthrough reaching 9.7% PCE when employing spiro-OMeTAD (2,2′,7,7′-tetakis(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene) as the hole-transporting material (HTM).3 This improvement marked the development of new organic small-molecule HTMs as one of the main research lines on PSCs.4–13 A second research line to improve the performance and stability of PSCs consists of researching new perovskite formulations by modifying both the cations and anions of the ABX3 stoichiometry. Such modifications generally lead to perovskites with improved characteristics such as reduced band gap and enhanced electronic properties as when substituting Pb2+ by the more environmentally friendly Sn2+. Replacement of the organic methylammonium (MA) cation by Cs+ or formamidinium (FA)14,15 or the halides (Cl− or Br− for I−) influences the stability, absorption, and electronic behavior.16,17 Formulations combining these modifications provide mixed compositional perovskites such as Cs0.17(MA0.83FA0.17)(I0.83Br0.17)3, MAPb(I1−xBrx)3, or [FAPbI ]0.85[MAPbBr ]0.15 with increased stability and efficiencies up to 22%.18–20 More recently, increased attention is being devoted to the development of the electron-transporting layer−1 by introducing fullerene derivatives,22–25 azacenes,26,27 and perylene diimides,28,29 among others, as n-type materials for replacing the typical inorganic oxide layer (TiO2, ZnO, SnO2, etc.).30–32 Another approach to the PSC research is the study of the effect of introducing certain additives to the active
layer, which has proved very successful in improving perovskite’s efficiency,33 long-term stability,34,35 water resistance,16,36 and stability against air.37

The two main design rules an efficient HTM must meet are (1) having the highest-occupied molecular orbital (HOMO) energetically located in between the valence band edge of the active layer and the cathode’s work function and (2) showing high hole conductivity and mobility. Meeting these two requisites ensures the efficient extraction of holes from the device. The last requirement is strongly dependent on the crystalline structure and the morphology of the HTM, properties which cannot, unfortunately, be predicted. Molecules bearing arylamines as electroactive functionalities have demonstrated to successfully meet the energetic alignment requisite when using perovskites as the active layer.3−11,38−40

In this sense, spiro-OMeTAD is the benchmark compound to which all HTMs are compared with due to its good performance in terms of efficiency, reproducibility, and stability. However, the high cost associated with its synthesis and purification stimulates chemists to develop new cheaper and more efficient HTMs. In this publication, we present two novel HTMs consisting of an anthra[1,9-bc:5,10-b’c’]-dithiophene (ADT) central core, showcasing two arylamine electroactive moieties appended to its frame, as depicted in Chart 1. Compared to the synthesis of the spiro-OMeTAD framework, the synthesis of ADT is a high-yield, three-step procedure from inexpensive starting materials. The PSCs fabricated employing ADT-DPA and ADT-TPA show moderate to high efficiencies, in the case of ADT-TPA being very similar to that of the spiro-OMeTAD reference.

#### RESULTS AND DISCUSSION

Materials Synthesis and Characterization. The synthesis of ADT was first reported by Wudl et al. in 1979 in a moderate to low yield (43%).41 However, the improved method described elsewhere42 allows achieving higher yields (75%). Thiolation of 1,5-dichloroanthracene-9,10-dione with mercaptoacetic acid in the presence of sodium ethoxide, manganese(II) oxide, and 15-crown-ether yields dicarboxylate anthraquinone 1 as an insoluble dark solid. Treatment of the
B3LYP/6-31G functional theory (DFT) calculations were carried out at the ADT-DPA third (Figure S1b). Differential scanning calorimetry measurements of ADT-TPA show melting point at 250.1 °C and glass transition at 131.7 °C for the second heating scan and 134.9 °C for the third. In the case of ADT-DPA, a melting point at 262.1 °C is found, along with a glass transition at 116.7 °C for the second heating scan and 119.4 °C for the third (Figure S1b).

To gain an insight into the structural and electronic properties of the ADT-DPA and ADT-TPA HTMs, density functional theory (DFT) calculations were carried out at the B3LYP/6-31G** level in the presence of CH₂Cl₂ as the solvent. The pendant DPA and TPA moieties, the ADT core, and the reference spiro-OMeTAD compound were also calculated for comparison purposes (see the Supporting Information for full computational details). The structures calculated for the HTMs show a very flat arrangement for ADT-TPA, with both TPA units lying almost in-plane with the ADT core, whereas the DPA moieties in ADT-DPA are almost orthogonal to the central ADT core (Figure S2). The analysis of the bond lengths computed for the ADT core (Figure S3) evidences the loss of the anthracene-like structural pattern: the external benzenes exhibit a delocalized aromatic structure with minimal C–C bond-order alternation (lengths in the 1.395–1.415 Å range), whereas the central benzene ring presents a more localized structure and acts as a bridge between the external rings with C–C distances of 1.448 and 1.466 Å. On the other hand, the fused thiophene rings preserve their characteristic single-double C–C bond-length alternation, with the edge C–C double bond length being 1.367 Å and the single and double bonds shared with the anthracene being 1.448 and 1.407 Å, respectively. Therefore, the ADT core can be assimilated to two benzothiophene units connected by single C–C bonds (1.466 Å). For the ADT-DPA and ADT-TPA molecules, the anchoring of the two DPA or TPA units hardly causes any substantial change in the bond lengths of the conjugated core, with the exception of the C–C and C–S thiophene bonds to which the DPA/TPA units are directly attached (Figure S3).

The electrochemical behavior of the new HTMs was studied by cyclic voltammetry measurements. As expected from the electron-rich nature of the arylamine moieties, both molecules show anodic activity (see Figure 1a). Compound ADT-DPA exhibits two well-defined oxidation waves ($E_{1/2}^{ox1} = 0.93$; $E_{1/2}^{ox2} = 1.25$ V vs. NHE), which contrasts with derivative ADT-TPA, showing a broad oxidation process comprising two waves at a sensibly lower potential ($E_{1/2}^{ox} = 0.74$ V). HOMO energy levels, estimated from the first oxidation potential, of $−5.18$ and $−5.37$ eV for ADT-DPA and ADT-TPA, respectively, are found in Table 1, which are similar to the value recorded for spiro-OMeTAD ($−5.16$ eV). The slightly deeper HOMO of derivative ADT-TPA allows a closer energy alignment with the valence band of the perovskite (ca. $−5.65$ eV), in turn yielding a higher open circuit potential.

### Table 1. Electrochemical and Photophysical Parameters of HTMs ADT-DPA and ADT-TPA

| HTM       | $E_{1/2}^{ox}$ [V] | $E_{\text{HOMO}}$ [eV] | $\lambda_{\text{max}}$ [nm] | $\rho_{\text{max}}$ [nm] | $E_{\text{LUMO}}$ [eV] |
|-----------|--------------------|------------------------|-----------------------------|-------------------------|------------------------|
| ADT-DPA   | 0.74               | $−5.18$                | 413                         | 476                     | 2.73                   | $−2.45$                |
| ADT-TPA   | 0.93               | $−5.37$                | 431                         | 547                     | 2.65                   | $−2.72$                |

$^a$Recorded versus normal hydrogen electrode (NHE). $^b$HOMO estimated as $E_{\text{HOMO}} = −4.44$ eV $− E_{1/2}^{ox}$. $^c$Optical band gap estimated from the intersection of the absorption and emission spectra. $^d$LUMO estimated as $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{inj}}$.

Figure 2 displays the frontier molecular orbitals calculated at the B3LYP/6-31G** level for the HTMs, their constituent fragments, and the reference compound spiro-OMeTAD. The HOMO of the ADT core ($−5.22$ eV) is significantly lower in energy than the HOMO levels computed for the DPA and TPA arylamines ($−4.72$ and $−4.77$ eV, respectively) in line with the weaker electron-donating character of the ADT moiety. The HOMOs of ADT-TPA ($−4.72$ eV) and ADT-DPA ($−4.71$ eV) retain almost the same energy as the parent arylamines, although spreading all over the whole molecules. In contrast, the lowest-occupied molecular orbital (LUMO) is mainly located over the ADT core for ADT-TPA ($−1.61$ eV) and slightly comprising the first neighboring phenyl ring of the TPA moieties in ADT-TPA ($−1.72$ eV). The energies calculated for the HOMO are close to that calculated for the reference spiro-OMeTAD ($−4.44$ eV). It is of note that an important and opposite charge transfer takes place from the peripheral DPA and TPA units to the sulfur-rich central core. ADT-DPA holds a total net charge of 0.21e in its core, whereas a charge of $−0.25e$ is predicted for the core of ADT-TPA. These compounds are therefore significantly polarized.

To gain a better insight into the oxidation process, the oxidized species (cations and dications) of ADT-DPA and ADT-TPA were calculated at the B3LYP/6-31G** level in CH₂Cl₂. Table S1 gathers the charges accumulated by the constituent fragments (central core and DPA and TPA units) as oxidation occurs. For ADT-DPA**, the charge for the radical cation species is withdrawn from the core (0.46e) and the DPA units (0.27e from each unit). For ADT-TPA**, a slightly smaller charge is removed from the core (0.36e), whereas 0.32e are extracted from each TPA unit. Upon further oxidation to the dication, the charge extracted resides on both the core (1.14e) and the DPA units (0.43e each) for ADT-TPA**, whereas it is mainly concentrated on the pendant TPA moieties (0.98e each) for ADT-TPA+ (Table S1). This indicates that oxidation mainly involves the TPA units in ADT-TPA, whereas it implies both the ADT core and the peripheral DPA units for ADT-DPA. It should be stressed that, for both ADT-DPA and ADT-TPA, the ionization energies (IEs) required for going from the neutral molecule to the cation (IE1) and from the cation to the dication (IE2) are predicted to have relatively close values. The IE1 and IE2 values for ADT-DPA (ADT-TPA) were computed to be 4.50 (4.58) and 5.14 (4.96) eV, respectively. The larger separation between the IE1 and IE2 values for ADT-DPA (0.64 eV) compared to ADT-TPA (0.38 eV) may account for the structured two-electron first oxidation wave observed for ADT-TPA that coalesce into a non-structured broad oxidation wave for ADT-DPA (Figure 1a). The second oxidation wave observed for the later at 1.25 V corresponds to the oxidation of the ADT core. Furthermore, the higher IE1 value predicted
for ADT-TPA is in agreement with the higher oxidation potential recorded for ADT-TPA compared to ADT-DPA (Table 1).

To evaluate the ability of ADT-DPA and ADT-TPA as HTMs, hole reorganization energies ($\lambda$) were computed at the B3LYP/6-31G** level in the gas phase (see the Supporting Information for full computational details). The $\lambda$ values estimated for ADT-DPA and ADT-TPA are 0.460 and 0.241 eV, respectively. The $\lambda$ values calculated for their constituting fragments are 0.193 eV for the ADT core and 0.309 and 0.274 eV for the DPA and TPA units, respectively. ADT-TPA therefore exhibits a $\lambda$ value intermediate between those of the ADT core and the TPA units, whereas the $\lambda$ value computed for ADT-DPA is higher than those of its constituting fragments and almost doubles that obtained for ADT-TPA.

ADT-TPA actually holds a relatively low reorganization energy in the range found for other excellent p-type semiconducting organic materials,\textsuperscript{37} although higher than that obtained for the benchmark compound spiro-OMeTAD (0.139 eV).\textsuperscript{28} Therefore, ADT-TPA is considered a better candidate than ADT-DPA as the HTM for PSC devices owing to its significantly smaller $\lambda$ value and appropriate energy level alignment with the valence band edge of the perovskite.

The novel HTMs show similar optical absorption patterns (Figure 1b and Table 1). Both ADT derivatives present a low-energy, intense (around $3 \times 10^4$ M$^{-1}$ cm$^{-1}$) absorption band peaking at 413 and 431 nm for ADT-DPA and ADT-TPA, respectively, with a small shoulder at ca. 360 nm. The room-temperature emission spectra display a featureless broad band centered at 476 and 547 nm for ADT-DPA and ADT-TPA,
respectively. Noticeably, ADT-TPA shows a large shift between the absorption and emission maxima of 130 nm.

A theoretical simulation of the absorption spectra of ADT-DPA and ADT-TPA (Figure S5) was performed based on the vertical energies and oscillator strengths calculated for the lowest-energy 80 singlet-excited electronic states (S) at the B3LYP/6-31G** time-dependent DFT level in CH₂Cl₂. The theoretical spectrum for ADT-DPA notably reproduces the shape of the experimental spectrum with two intense bands centered at 468 and 280 nm and a shoulder between both bands (362 nm). A similar pattern with two intense absorption bands at 481 and 310 nm and a weaker, less-visible shoulder (ca. 350 nm) is predicted for ADT-TPA. Theoretical calculations therefore reproduce the red shift experimentally observed in passing from ADT-DPA to ADT-TPA (Figure 1b). For both molecules, the lowest-energy band is due to the S → S electronic transition mainly resulting from the HOMO → LUMO monoelectronic excitation (see Figure S5 and Table S2). The shoulder is associated with the S → S electronic transitions for ADT-DPA, and to the S → S and S → S electronic transitions for ADT-TPA. These transitions are of a π → π* nature and largely involve excitations centered on the core ADT moiety (Table S2 and Figure S6).

Solar Cell Fabrication and Characterization. The new compounds ADT-DPA and ADT-TPA were investigated as hole-extracting layers in PSCs and compared with the benchmark molecule spiro-OMeTAD. Devices with a conventional n-i-p configuration were fabricated from a stack of FTO/c-TiO₂/m-TiO₂/perovskite/HTM/Au (experimental details can be found in the Supporting Information). A mixed-ion perovskite with the (FAPbI₃)₀.₈₅(MAPbBr₃)₀.₁₅ composition was used as the light-absorbing material. The new HTMs as well as spiro-OMeTAD were chemically doped using tert-butylpyridine (Tbp), lithium bis(trifluoromethanesulfonyl)imide, and tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III)tris[bis(trifluoromethane)sulfonimide] (FK 209 Co(III)-TFSI) as additives to increase their carrier mobility. The efficiencies of the fabricated devices were measured under 1 sun (100 mW cm⁻²) simulated sunlight. The current density/voltage (J/V) curves of the champion devices are shown in Figure 3a. The energy levels of the individual solar cell components are displayed in Figure 3b, and a SEM cross-sectional image of a finished device with ADT-TPA as the HTM is shown in Figure 3c. The thicknesses of the HTM layers for ADT-TPA and ADT-DPA were estimated to be around 90 and 40 nm, respectively.

Devices with ADT-TPA as the HTM were shown to perform significantly better than those with ADT-DPA. Reverse scans of ADT-TPA yielded efficiencies up to 17.6%, close to what was observed with the spiro-OMeTAD reference cell (Figure S8). To quantify the hysteresis between reverse and forward scans, the hysteresis index (HI) = (PCE forward − PCE reverse)/PCE reverse was calculated.⁴⁴ For ADT-TPA, contributions from hysteresis (HI = 3.5%) were found to be small, much better than those observed for the reference spiro-OMeTAD (HI = 6.1%). The short circuit current (JSC) larger than 20 mA cm⁻² was further confirmed by external quantum efficiency (EQE) measurements, as shown in Figure 4. Devices with ADT-DPA, however, show a significantly reduced open-circuit voltage (VOC) as well as a lower short-circuit current. Best efficiencies with ADT-DPA are therefore only 12.8%, measured in the reverse scan direction, showing a more pronounced hysteresis (HI = 8.6%) behavior. The under-performance of ADT-DPA devices with respect to ADT-TPA ones was initially attributed to poor layer formation: a cross-sectional image (Figure S9) unveils the presence of pin-holes that allow direct contact of the active layer with the gold electrode. These defects are suspected to be caused by the low solubility of ADT-DPA in chlorobenzene, the solvent employed for its deposition onto the perovskite layer. However, steady-state photoluminescence (PL) shows that both HTMs are able to effectively quench the PL of the perovskite (see Figure S10), which is indicative of interfacial hole transfer. Additionally, the process was monitored by time-resolved PL. The dynamics associated with the PL decay are consistent with a biexponential fit, where both spiro-OMeTAD and ADT-TPA show similar time constants, whereas ADT-DPA follows a much steeper decay (Figure S11). These results show that the new molecules can effectively quench the PL, thus representing efficient hole-transfer materials, similar in function to spiro-OMeTAD. Furthermore, the interfacial dynamics confirm the favorable hole transfer as it should be expected from the relative energy position of the HOMO level of the HTMs. One of the main critical issues of PSCs is that related to their stability in operational conditions.⁴⁵

The study of our ADT-based devices under maximum-power-point-tracking allowed to monitor their stability at 1 sun illumination for up to 40 h compared to devices based on spiro-OMeTAD (Figure S12). ADT-TPA shows a dramatic efficiency drop after the first 10 h of operation to thereafter sustain an operation stability over 30% of the original values after 40 h. In comparison, devices based on spiro-OMeTAD maintain 90–100% of the original values of efficiency after 40 h, while those based on ADT-TPA show a loss in efficiency from 80 to 50% in 40 h. Despite the initial decrease, a gradual recuperation of the performance was observed, which might be correlated with the TPA content. Thermal stability of the solar cells was explored keeping the devices at 85 °C with a relative humidity of 20% in air conditions for up to 120 min (Figure S13). Initially, a performance decrease associated with the inter-penetration of spiro-OMeTAD and gold electrodes was observed; then, after 120 min, the performance of the PSCs dropped to 39% (Spiro), 30% (TPA), and 18% (DPA) of the initial efficiency, respectively.

To compare the electrical properties of the different HTMs, conductivity measurements on substrates having interdigitating gold electrodes were performed. The HTMs were deposited...
using the same conditions as for the devices using 6 mol % FK209 as the dopant. A semilogarithmic representation of the current/voltage (I/V) curves and the corresponding conductivity values are shown in Figure 5. Spiro-OMeTAD was shown to have the largest conductivity ($\sigma = 1.5 \times 10^{-4}$ S cm$^{-1}$) closely followed by ADT-TPA ($\sigma = 4.3 \times 10^{-5}$ S cm$^{-1}$). Coherent with its poor performance in devices, HTM ADT-DPA showed conductivity ($\sigma = 7.6 \times 10^{-7}$ S cm$^{-1}$) that is 2 orders of magnitude lower than that of ADT-TPA. These results are consistent with the reorganization energies calculated theoretically, from which ADT-DPA and ADT-TPA show $\lambda$ values (0.460 and 0.241 eV, respectively) that are roughly 3.5 and 2 times higher than that of spiro-OMeTAD (0.139 eV). Moreover, the defect concentration of the hole-transporting layer was estimated from capacitance (0.139 eV). Moreover, the defect concentration of the hole-roughly 3.5 and 2 times higher than that of spiro-OMeTAD calculated theoretically, from which calculations, plotting the DoS frequency measurements and density of states (DoS) orders of magnitude lower than that of ADT-TPA closely followed by ADT-DPA. Coherent with its poor performance in devices, HTM ADT-DPA shows significantly lower reorganization energy for ADT-TPA that also favors hole extraction and conductivity.

**EXPERIMENTAL SECTION**

Related materials, solvents, instruments, and detailed experimental and computational procedures can be obtained from the Supporting Information.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c05890.

- Experimental section; synthetic details and characterization; thermal properties; computational details; device fabrication and characterization; and $^1$H NMR, $^{13}$C NMR, and HRMS spectra (PDF)

**AUTHOR INFORMATION**

Corresponding Authors

José Santos — Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Madrid 28040, Spain; orcid.org/0000-0002-9702-2315; Email: jose.santos@imdea.org; http://www.nazariomartingroup.com/

Mohammad Khaja Nazeeruddin — Group for Molecular Engineering of Functional Materials, EPFL VALAIS, Sion 1951, Switzerland; orcid.org/0000-0001-5955-4786; Email: mdkhaja.nazeeruddin@epfl.ch

Enrique Ortiz — Instituto de Ciencia Molecular, Universidad de Valencia, Paterna 46980, Spain; orcid.org/0000-0001-9544-8286; Email: enrique.orti@uv.es

Nazario Martin — Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Madrid 28040, Spain; IMDEA-Nanociencia, Ciudad Universitaria de Cantoblanco, Madrid 28049, Spain; orcid.org/0000-0002-5355-1477; Email: nazmar@ucm.es

Authors

Joaquín Calbo — Instituto de Ciencia Molecular, Universidad de Valencia, Paterna 46980, Spain; orcid.org/0000-0003-4729-0757

Rafael Sandoval-Torres — Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Madrid 28040, Spain

Inés García-Benito — Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Madrid 28040, Spain

Hiroyuki Kanda — Group for Molecular Engineering of Functional Materials, EPFL VALAIS, Sion 1951, Switzerland; orcid.org/0000-0002-0327-8775

Iwan Zimmermann — Group for Molecular Engineering of Functional Materials, EPFL VALAIS, Sion 1951, Switzerland; orcid.org/0000-0002-6183-2690

Juan Aragó — Instituto de Ciencia Molecular, Universidad de Valencia, Paterna 46980, Spain; orcid.org/0000-0002-0415-9946

Figure 5. Semilogarithmic current/voltage plots of spiro-OMeTAD and ADT derivatives spin-coated onto substrates having interdigitating gold electrodes with a channel length of 2.5 µm. The calculated conductivity values are shown.
Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.1c05890

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
(1) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photo voltaic Cells. J. Am. Chem. Soc. 2009, 131, 6050–6051.
(2) The NREL Online. 2021, https://www.nrel.gov/pv/assets/pdfs/pv- efficiencies-07-17-2018.pdf (accessed March, 2021), not published yet results from Korea Research Institute of Chemical Technology (KRICT)/MIT.
(3) Kim, H. S.; Lee, C. R.; Im, J. H.; Lee, K. B.; Moehl, T.; Marchioro, A.; Moon, S. J.; Humphrey-Baker, R.; Yum, J. H.; Moser, J. E.; Grätzel, M.; Park, N. G. Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%. Sci. Rep. 2012, 2, 591.
(4) Ganesan, P.; Fu, K.; Gao, P.; Raabe, I.; Schenk, K.; Scopelliti, R.; Luo, J.; Wong, L. H.; Grätzel, M.; Nazeeruddin, M. K. A Simple Spiral: Small-Molecule Type Hole Transporting Material for Efficient Perovskite Solar Cells. Energy Environ. Sci. 2015, 8, 1986–1991.
(5) Bi, D.; Xu, B.; Gao, P.; Sun, L.; Grätzel, M.; Hagfeldt, A. Facile Synthesized Organic Hole Transporting Material for Perovskite Solar Cell with Efficiency Of 19.8%. Nano Energy 2016, 23, 138–144.
(6) Wang, Y.-K.; Yuan, Z.-C.; Shi, G.-Z.; Li, Y.-X.; Li, Q.; Hui, F.; Sun, B.-Q.; Jiang, Z.-Q.; Liao, L.-S. Dopant-Free Spiro-Triphenylamine/Fluorene as Hole-Transporting Material for Perovskite Solar Cells with Enhanced Efficiency and Stability. Adv. Funct. Mater. 2016, 26, 1375–1383.
(7) Saliba, M.; Orlandi, S.; Matsu, T.; Aghazada, S.; Cavazzini, M.; Correa-Baena, J.-P.; Gao, P.; Scopelliti, R.; Mosconi, E.; Dahmen, K.-H.; De Angelis, F.; Abate, A.; Hagfeldt, A.; Pozzi, G.; Graetzel, M.; Nazeeruddin, M. K. A Molecularly Engineered Hole-Transporting Material for Efficient Perovskite Solar Cells. Nat. Energy 2016, 1, 15017.
(8) Zimmermann, I.; Urieta-Mora, J.; Gratie, P.; Araó, J.; Grancini, G.; Molina-Ontoria, A.; Ortí, E.; Martin, N.; Nazeeruddin, M. K. High-Efficiency Perovskite Solar Cells Using Molecularly Engineered, Thiophene-Rich, Hole-Transporting Materials: Influence of Alkyl Chain Length on Power Conversion Efficiency. Adv. Energy Mater. 2017, 7, 1601674.
(9) García-Benito, I.; Zimmermann, I.; Urieta-Mora, J.; Araó, J.; Molina-Ontoria, A.; Ortí, E.; Martin, N.; Nazeeruddin, M. K. Isomerism Effect on the Photovoltaic Properties of Benzothriothiophene-Based Hole-Transporting Materials. J. Mater. Chem. A 2017, 5, 8317–8324.
(10) Sandoval-Torrientes, R.; Zimmermann, I.; Calbo, J.; Aragó, J.; Santos, J.; Ortí, E.; Martin, N.; Nazeeruddin, M. K. Hole Transporting Materials Based on Benzothiophene and Dithienopyrrole Cores for Efficient Perovskite Solar Cells. J. Mater. Chem. A 2018, 6, 5944–5951.
(11) Jeon, N. J.; Na, H.; Jung, E. H.; Yang, T.-Y.; Lee, Y. G.; Kim, G.; Shin, H.-W.; Il Seok, S.; Lee, J. S.; Seo, J. A Fluorene-Terminated Hole-Transporting Material for Highly Efficient and Stable Perovskite Solar Cells. Nat. Energy 2018, 3, 682–689.
(12) For a recent review on HTMs see: Urieta-Mora, J.; García-Benito, I.; Molina-Ontoria, A.; Martin, N. Hole Transporting Materials for Perovskite Solar Cells: A Chemical Approach. Chem. Soc. Rev. 2018, 47, 8541–8571.
(13) Calió, L.; Kazim, S.; Grätzel, M.; Ahmad, S. Hole-Transport Materials for Perovskite Solar Cells. Angew. Chem., Int. Ed. 2016, 55, 14522–14545.
(14) Stoumpos, C. C.; Malliakas, C. D.; Kanatzidis, M. G. Semiconducting Tin and Lead Iodide Perovskites with Organic Cations: Phase Transitions, High Mobilities, and Near-Infrared Photoluminescent Properties. Inorg. Chem. 2013, 52, 9019–9038.
(15) Eperon, G. E.; Stranks, S. D.; Menelaou, C.; Johnston, M. B.; Herz, L. M.; Snaith, H. J. Formamidinium Lead Trihalide: A Broadly Tunable Perovskite for Efficient Planar Heterojunction Solar Cells. Energy Environ. Sci. 2014, 7, 982–988.
(16) Calabrese, J.; Jones, N. L.; Harlow, R. L.; Herron, N.; Thorn, D. L.; Wang, Y. Preparation and Characterization of Layered Lead Halide Compounds. J. Am. Chem. Soc. 1991, 113, 2328–2330.
(17) Noh, J. H.; Im, S. H.; Heo, J. H.; Mandal, T. N.; Seok, S. I. Chemical Management for Colorful, Efficient, and Stable Inorganic-Organic Hybrid Nanostructured Solar Cells. Nano Lett. 2013, 13, 1764–1769.
(18) Yang, W. S.; Park, B.-W.; Jung, E. H.; Jeon, N. J.; Kim, Y. C.; Lee, D. U.; Shin, S. S.; Seo, J. J.; Kim, E. K.; Noh, J. H.; Seok, S. I. Iodide management in formamidinium-lead-halide-based perovskite layers for efficient solar cells. Science 2017, 356, 1376–1379.
(19) Saliba, M.; Matsu, T.; Seo, J.-Y.; Domanski, K.; Correa-Baena, J.-P.; Nazeeruddin, M. K.; Zakeeruddin, S. M.; Tress, W.; Abate, A.; Hagfeldt, A.; Grätzel, M. Cesium-Containing Triple Cation Perovskite Solar Cells: Improved Stability, Reproducibility and High Efficiency. Energy Environ. Sci. 2016, 9, 1989–1997.
(20) Jeon, N. J.; Noh, J. H.; Yang, W. S.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I. Compositional Engineering of Perovskite Materials for High-Performance Solar Cells. Nature 2015, 517, 476–480.
(21) Mahmood, K.; Sarwar, S.; Mehran, M. T. Current Status of Electron Transport Layers in Perovskite Solar Cells: Materials and Properties. RSC Adv. 2017, 7, 17044–17062.
(22) Zhong, Y.; Munir, M.; Balawi, A. H.; Sheikh, A. D.; Yu, L.; Tang, M.-C.; Hu, H.; Laguì, F.; Amassian, A. Mesostructured Fullerene Electrodes for Highly Efficient n-i-p Perovskite Solar Cells. ACS Energy Lett. 2016, 1, 1049–1056.
(23) Zhang, F.; Shi, W.; Luo, J.; Pellet, N.; Yi, C.; Li, X.; Zhao, X.; Dennis, T. J. S.; Li, X.; Wang, S.; Xiao, Y.; Zakeeruddin, S. M.; Bi, D.; Grätzel, M. Isomer-Pure Bis-PCBM-Assisted Crystal Engineering of Perovskite Solar Cells Showing Excellent Efficiency and Stability. Adv. Mater. 2017, 29, 1606806.
(24) Sandoval-Torrientes, R.; Pascual, J.; García-Benito, I.; Collavini, J.; Kosta, I.; Tena-Zaera, R.; Martin, N.; Delgado, J. L. Modified Fullerenes for Efficient Electron Transport Layer-Free Perovskite/Fullerene Blend-Based Solar Cells. ChemSusChem 2017, 10, 2023–2030.
(25) For a review on fullerene based ETls see: Pascual, J.; Delgado, J. L.; Tena-Zaera, R. Physicochemical Phenomena and Application in Solar Cells of Perovskite/Fullerene Films. J. Phys. Chem. Lett. 2018, 9, 2893–2902.
(26) Gu, P.-Y.; Wang, N.; Wu, A.; Wang, Z.; Tian, M.; Fu, Z.; Sun, X. W.; Zhang, Q. An Azaacene Derivative as Promising Electron-
Materials for Perovskite Solar Cells. Chem.—Asian J. 2016, 11, 2135–2138.

(27) Zhao, D.; Zhu, Z.; Kuo, M. Y.; Chueh, C. C.; Jen, A. K. Y. Hexazatriaraphenylene Derivatives: Efficient Electron-Transporting Materials with Tunable Energy Levels for Inverted Perovskite Solar Cells. Angew. Chem., Int. Ed. 2016, 55, 8999–9003.

(28) Zhang, H.; Xue, L.; Han, J.; Fu, Y. Q.; Shen, Y.; Zhang, Z.; Li, Y.; Wang, M. New Generation Perovskite Solar Cells with Solution-Processed Amino-Substituted Perylene Diamide Derivative as Electron-Transport Layer. J. Mater. Chem. A 2016, 4, 8724–8733.

(29) Jiang, K.; Wu, F.; Yu, H.; Yao, Y.; Zhang, G.; Zhu, L.; Yan, H. A Perylene Diimide-Based Electron Transport Layer Enabling Efficient Inverted Perovskite Solar Cells. J. Mater. Chem. A 2018, 6, 16868–16873.

(30) Zuo, L.; Gu, Z.; Ye, T.; Fu, W.; Wu, G.; Li, H.; Chen, H. Enhanced Photovoltaic Performance of CH3NH3PbI3 Perovskite Solar Cells through Interfacial Engineering Using Self-Assembling Monolayer. J. Am. Chem. Soc. 2015, 137, 2674–2679.

(31) Azmi, R.; Hadmojo, W. T.; Sinaga, S.; Lee, C.-L.; Yoon, S. C.; Jung, I. H.; Jang, S.-Y. High-Efficiency Low-Temperature ZnO Based Perovskite Solar Cells Based on Highly Polar, Nonwetting Self-Assembled Molecular Layers. Adv. Energy Mater. 2018, 8, 1701683.

(32) Song, J.; Zheng, E.; Bian, J.; Wang, X.-F.; Tian, W.; Sanehira, Y.; Miyasaka, T. Low-temperature SnO2-based electron selective contact for efficient and stable perovskite solar cells. J. Mater. Chem. A 2015, 3, 10837–10844.

(33) Geoffroy, C.; Grana, E.; Bessho, T.; Almosni, S.; Tang, Z.; Sharma, A.; Kinoshiba, T.; Awai, F.; Cloutet, E.; Toupance, T.; Segawa, H.; Hadziioannou, G. p-Doping of a Hole Transport Material via a Poly(ionic liquid) for over 20% Efficiency and Hysteresis-Free Perovskite Solar Cells. ACS Appl. Energy Mater. 2020, 3, 1393–1401.

(34) Feng, J.; Zhu, X.; Yang, Z.; Zhang, X.; Niu, J.; Wang, Z.; Zuo, S.; Priya, S.; Liu, S.; Yang, D. Record Efficiency Stable Flexible Perovskite Solar Cell Using Effective Additive Assistant Strategy. Adv. Mater. 2018, 30, 1801418.

(35) Christians, J. A.; Schulz, P.; Tinkham, J. S.; Scholemer, T. H.; Harvey, S. P.; Tremolet de Villers, B. J.; Sellinger, A.; Berry, J. J.; Luther, J. M. Tailored Interfaces of Unencapsulated Perovskite Solar Cells for >1,000 Hour Operational Stability. Nat. Energy 2018, 3, 68–74.

(36) Li, L.; Jin, X.; Liu, N.; Chen, Q.; Zhang, W.-B.; Zhou, H. Efficient Moisture-Resistant Perovskite Solar Cell With Nanostructure Featuring 3D Amine Motif. Sol. RRL 2018, 2, 1800069.

(37) Hsu, H.-L.; Hsiao, H.-T.; Jiang, T.-Y.; Jiang, B.-H.; Chen, S.-C.; Jeng, R.-J.; Chen, C.-P. Carbon Nanodot Additives Realize High-Performance Air-Stable p–i–n Perovskite Solar Cells Providing Efficiencies of up to 20.2%. Adv. Energy Mater. 2018, 8, 1803233.

(38) Huang, C.; Fu, W.; Li, C.-Z.; Zhang, Z.; Qiu, W.; Shi, M.; Heremans, P.; Jen, A. K.-Y.; Chen, H. Dopant-Free Hole-Transporting Material with a C60 Symmetrical Truxene Core for Highly Efficient Perovskite Solar Cells. J. Am. Chem. Soc. 2016, 138, 2528–2531.

(39) Urieta-Mora, J.; García-Benito, I.; Zimmermann, I.; Aragó, J.; Molina-Ontoria, A.; Ortí, E.; Martin, N.; Nazeeruddin, M. K. Tetrasubstituted Thiophene[3,2-b]thiophenenes as Hole-Transporting Materials for Perovskite Solar Cells. J. Org. Chem. 2020, 85, 224–233.

(40) Duan, L.; Chen, Y.; Jia, J.; Zong, X.; Sun, Z.; Wu, Q.; Xue, S. Dopant-Free Hole-Transport Materials Based on 2,4,6-Triarylpypyridine for Inverted Planar Perovskite Solar Cells. ACS Appl. Energy Mater. 2020, 3, 1672–1683.

(41) Wudl, F.; Hadden, R. C.; Zellers, E. T.; Bramwell, F. B. 3,5-Bis(benzofuran-4-yl)thiophene. J. Org. Chem. 1979, 44, 2491–2493.

(42) Brown, C. T.; Chopra, N.; Knittel, C. R.; Mathai, M.; Seshari, V.; Wang, J.; Woodworth, B. Hole Transport Compositions and Related Devices and Methods (1). WO2012003485A3, Jan 5, 2012.

(43) Rakstys, K.; Saliba, M.; Gao, P.; Gratia, P.; Kamarakas, E.; Paek, S.; Jankauskas, V.; Nazeeruddin, M. K. Highly Efficient Perovskite Solar Cells Employing an Easily Attainable Bifuoroenyl-