**ABSTRACT:** To attain commercial viability, perovskite solar cells (PSCs) have to be reasonably priced, highly efficient, and stable for a long period of time. Although a new record of a certified power conversion efficiency (PCE) value over 25% was achieved, PSC performance is limited by the lack of hole-transporting materials (HTMs), which extract positive charges from the light-absorbing perovskite layer and carry them to the electrode. Here, we report spirobifluorene-based HTMs with finely tuned energy levels, high glass-transition temperature, and excellent charge mobility and conductivity enabled by molecularly engineered enamine arms. HTMs are synthesized using simple condensation chemistry, which does not require costly catalysts, inert reaction conditions, and time-consuming product purification procedures. Enamine-derived HTMs allow the fabrication of PSCs reaching a maximum PCE of 19.2% and stability comparable to spiro-OMeTAD. This work demonstrates that simple enamine condensation reactions could be used as a universal path to obtain HTMs for highly efficient and stable PSCs.

**INTRODUCTION**

The perovskite materials used in solar cells, i.e., perovskite solar cells (PSCs), and APbX₃ (A = methylammonium (MA), formamidinium (FA), caesium (Cs); X = Br, I) have remarkable properties, such as high absorption coefficients, long carrier diffusion lengths, small exciton binding energies, and high charge carrier mobilities. Most highly efficient PSCs utilize an n-type layer of mesoporous TiO₂ and a p-type layer of spiro-OMeTAD in an n–i–p device configuration, where perovskite materials are used as light absorbers. With the increased quality of perovskite films, further optimization of other layers to improve the overall solar cell performance is needed. Specifically, there is a renewed interest in identifying hole-transporting materials (HTMs) other than spiro-OMeTAD that can yield high power conversion efficiency (PCE).

Since the first report of an HTM in solid-state dye-sensitized solar cells 2 decades ago, the organic semiconductor 2,2′,7,7′-tetrakis-(N,N′-di-p-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD) has revolutionized the field and has been selected as the state-of-the-art benchmark. Two decades have passed, yet spiro-OMeTAD still prevails among other HTMs in the field of PSCs, and despite its high cost (~$250/g), it is commonly used as a highly efficient reference material for research studies. The wide availability of spiro-OMeTAD due to its low cost and practical synthesis methods has been fundamental to the rapid advancements in PSC research. However, the cost-effectiveness of spiro-OMeTAD has limited its widespread adoption for commercial applications.

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common $sp^3$-hybridized atom. Several groups have studied central 9,9′ spirobifluorene-linked HTMs including dimethyl-fluorienyl-, ethylcarbazolyl-, and fluorinated methoxyphenyl-terminated compounds, which have been recently reported by Seo,18 Chen,19 and Yang,20 respectively. However, the main focus is still directed on the development of new central spiro-cores such as spiro[fluorene-9,9′-xanthene],21−25 spirobisacridine,26 thiophene-containing spiro cores,27−29 and other spiro-type derivatives.30,31 However, the peripheral part is equally or of even more importance in fine tuning the properties of the HTM.32,33 Generally, such spiro-centered HTMs are designed by linking prebrominated spiro core species with diphenylamine or borylated triphenylamine, both having electron-rich methoxy groups using $C−N$ or $C−C$ cross-coupling reactions, respectively. These reactions demand severe procedures that result in several disadvantages including inert reaction conditions, costly transition-metal catalysts, and time-consuming purification procedures due to the inherent formation of side products. Moreover, residues of metal catalysts remain in the HTL, which act as traps, deteriorating charge-transporting properties and negatively affecting the performance of the resulting devices.34,35 Therefore, the hunt is now on for new organic semiconductors that are prepared by simple, cost-effective, and green chemistry without sacrificing the efficiency.36,37 In this sense, enamine condensation is promising to eliminate the use of palladium-catalyzed reactions since the only byproduct is water and cost-ineffective catalysts are not involved. In addition, greatly simplified product workup and purification significantly minimize the cost of the final product.38−40

Herein, we present a condensation-based spirobifluorene enamine family. The influence of different substitutions in the central spirobifluorene core going from single- to multiarmed enamines was revealed, showing that a higher degree of substitution has several advantages. First, the perpendicular arrangement of the two overcrowded enamine-based molecular halves leads to a high steric demand of the resulting rigid structure, efficiently suppressing molecular interactions. Furthermore, compound V1307 with a larger globular structure, higher molecular weight, and small intermolecular cohesion results in a high stability of the amorphous state. Comparing directly the dimethoxydiphenylamine- and bis(dimethoxydiphenylamine)-donating fragments of spiro-OMeTAD and V1307, respectively, it is found that the latter has some merits. First, bis(dimethoxydiphenylamine) being a less strong donor results in the stabilized HOMO values.

Figure 1. Schematic comparing cross-coupling and condensation reactions for the synthesis of spiro-OMeTAD and novel enamine HTMs.
Second, the more pronounced and higher degree of conjugation in enamine arms results in the better charge transport through V1307, a more densely packed layer. These advantages made novel enamine-derived spirobiuorene HTMs promising candidates for their successful application in PSCs, reaching a photovoltaic performance of up to 19.2% with comparable stability. With this, we demonstrate the simple enamine condensation chemistry as a universal approach to obtain highly efficient and stable HTMs.

Results and Discussion

Figure 1 presents the chemical structures of the parent spiro-OMeTAD and enamine-based analogues (V1307, V1305, V1306, and V1308). A series of four new HTMs containing a well-known spirobiuorene core with enamine arms were obtained simply by condensing aminated precursors with 2,2-bis(4-methoxyphenyl)acetaldehyde. The condensation reaction was carried out under ambient conditions, and the only byproduct is water, which is continuously separated using a Dean–Stark trap that accelerates the formation of the final product. Detailed synthetic protocols and full characterization of the compounds (NMR spectroscopy, mass spectrometry, and elemental analysis) are described in the Supporting Information. To assess the synthesis costs of the enamine condensation reaction in comparison with the regular cross-coupling reaction, we calculated the costs on a lab-scale synthesis (Table S1). The evaluated cost of V1307 is $37/g, which is much less than the cost of spiro-OMeTAD (~$92/g).

Thermogravimetric analysis suggests that novel HTMs start to decompose at around 400 °C (Figure S1), which is far above the temperature for conventional device operation. Differential scanning calorimetry measurements (Figure S2) indicate that V1305, V1306, and V1308 could exist in both crystalline and amorphous states similar to spiro-OMeTAD.

Interestingly, V1307 is fully amorphous and has the highest glass-transition temperature ($T_g$) of 169 °C, which should result in the improved quality of the V1307 layers. We also note that all synthesized HTMs have higher $T_g$ than spiro-OMeTAD (124 °C), meaning that the introduction of enamine fragments improves the morphological stability.

Gaussian09 software was used for simulation purposes to establish the most probable molecular geometries of V1305, V1306, V1307, and V1308 with their corresponding absorption spectra. Ground state geometry optimization was performed by means of the density functional theory method with B3LYP and 6-31G basis sets without polarization functions, and the predicted molecular structures are presented in Figure S3. As expected, two fluorene core fragments (F1>C<F2) are connected through the carbon atom having a perpendicular orientation. Due to the presence of the double bonds in the enamine chain [C=CH=N=CH=CH=C], orientation of substituents is chaotic and a large number of different possible positions are allowed. However, the most probable orientation is related to the V-shaped structure, when one methoxyphenyl fragment of F1 is oriented to the end of F2 (see Figure S3, V1305). Similar enamine branch orientations could be found in V1306, V1307, and V1308. Interestingly, comparing both four-armed V1307 and spiro-OMeTAD, several differences in the molecular orientation are observed, i.e., well-ordered and dual-axed perpendicular symmetry of spiro-OMeTAD is damaged since the fluorenes in V1307 are not completely perpendicular, and they are not flat anymore due to the chaotic arrangement of enamine substituents resulting in the fully amorphous morphology of V1307.

The ultraviolet–visible absorption (UV–vis) spectra in THF solutions of V1305, V1306, V1307, and V1308 are shown in Figure 2a. All spiro-enamines possess two significant absorption bands at around 260 and 380 nm. The less intense absorption at shorter wavelengths corresponds to localized π–π* transitions. Longer wavelengths are observed for more intensive delocalization from the conjugated scaffold and are assigned to n–π* transitions. The change in the number and the position of enamine arms in the system has significantly influenced the absorption. While the increasing number of enamine arms shifts the absorption hyperchronically (V1305 < V1306 < V1308 < V1307), the increased conjugation in V1307 and V1308, where fluorene is substituted on both sides, also resulted in the bathochromic shift around 35 nm. The optical gaps ($E_g$) were evaluated from the intersection of absorption and photoluminescence (PL) spectra of thin films and were estimated to be similar for all of the compounds at around 2.85 eV (Figure S6).
The solid-state ionization potentials ($I_p$) of V1305, V1306, V1307, and V1308, and spiro-OMeTAD were determined using photoemission spectroscopy in air (PESA) of the thin films to assess the HOMO energy level of spiro-enamine HTMs (Figure S7). $I_p$ values of V1305, V1306, V1307, and V1308 were found to be 5.33, 5.37, 5.46, and 5.46 eV, respectively, which are significantly stabilized compared to those of spiro-OMeTAD (5.00 eV). Based on the solid-state optical gap and $I_p$ values, we calculated the electron affinities ($E_a$) to be 2.43, 2.53, 2.63, and 2.68 eV for V1305, V1306, V1307, and V1308, respectively. Importantly, the electron affinities are smaller compared with the conduction band energy of the perovskite (−4.10 eV); therefore, effective electron blocking from the perovskite to the electrode should be ensured.

Xerographic time-of-flight measurements were used to determine the charge mobility of the V-series layers. Dependencies of hole drift mobility on the electric field strength are shown in Figure 2b. V1308 and V1307 exhibited the highest zero-field hole-drift mobility ($\mu_h$) among the series with the values of $9.4 \times 10^{-4}$ and $6.4 \times 10^{-4}$ cm$^2$/Vs, respectively, both outperforming spiro-OMeTAD ($\mu_h = 1.3 \times 10^{-4}$ cm$^2$/Vs). In addition, the lateral thin film conductivity of the V-series layers was measured with organic field-effect transistors (OFETs) (Figure S8). Similar to the result of the hole mobility measurement, V1307 and V1308 showed a higher conductivity ($1.4 \times 10^{-3}$ and $2.9 \times 10^{-3}$ S cm$^{-1}$, respectively) than V1305 ($3.9 \times 10^{-6}$ S cm$^{-1}$) and V1306 ($6.7 \times 10^{-6}$ S cm$^{-1}$). The conductivity of the doped spiro-OMeTAD as a reference was determined to be $1.0 \times 10^{-3}$ S cm$^{-1}$. The conductivity trend obtained for the V-series was found to be directly correlated with the degree of conjugation of the molecules. The fact that V1307 has the higher hole mobility and
conductivity value between the V-series and spiro-OMeTAD can be attributed to the higher degree of conjugation in enamine arms of V1307.45-47 The thermal, optical, and photoelectrical properties of the spiro-enamines are summarized in Table 1.

Steady-state PL was evaluated in samples with glass/perovskite and glass/perovskite/HTM layouts to determine their hole extraction properties in PSCs (Figure 3a). The PL spectra show that the hole transfer between V1307 and V1308 HTMs and perovskite is more efficient than that between V1305 and V1306. A slight quenching effect is observed in V1305 and V1306, which is in good agreement with the lowest hole drift mobility values (5.4 x 10^-6 cm^2/Vs for V1305 and 1.7 x 10^-5 cm^2/Vs for V1306). This quenching is enhanced with the use of spiro-OMeTAD, V1307, and V1308 HTMs that have higher hole mobility values (1.3 x 10^-4, 6.4 x 10^-4, and 9.4 x 10^-4 cm^2/Vs) due to more efficient hole transfer between perovskite and the corresponding HTM.

Fabrication of n-i-p solar cells was carried out with the device layout FTO/c-TiO2/m-TiO2/SnO2/perovskite/HTM/Au by spin-coating, except for the top electrode, deposited by thermal evaporation. The perovskite composition used was the triple-cation perovskite [(FAP-b13 )0.87(MAPb(Br)3)0.13]0.02(CsPbI3)0.08, and the HTM is doped with the bis(trifluoromethylsulfonyl)imide lithium salt (LiTFSI) and cobalt(III)-tris(bis(trifluoromethylsulfonyl)-imide). tert-Butylpyridine (tBP) was also added to the HTM solution to improve the HTM morphology and increase the LiTFSI solubility.48 The energy diagram of the device is shown in Figure 3b, and the detailed preparation process is described in the Methods section. Cross-sectional and top-view scanning electron microscopy (SEM) images were obtained to determine the thickness and morphology of the HTM, respectively (Figures S9 and S10). The HTM thickness is 180 nm for spiro-OMeTAD-based devices; 80 nm for devices containing V1305, V1306, and V1307; and 140 nm for devices fabricated with V1308.

The current–voltage (J–V) characteristics of the most efficient devices are presented in Figure 3c, and their corresponding PV parameters are extracted and shown in Table 2. The most efficient devices containing V1305, V1307, and V1308 have similar PCE values of 19.0%, 19.2%, and 19.1%, respectively. The corresponding external quantum efficiency (EQE) and the integrated current density are shown in Figure S11. The analysis of the statistical data presented in Figure S12 and Table S4 confirms the correlation between hole-drift mobility and device performance, and being the most efficient, the devices containing the HTM with higher hole mobility values follow the order: V1306 < V1305 < V1307 < V1308.49

Although the use of HTMs with deeper HOMO levels is, in principle, beneficial for the device performance due to larger Voc values,33,50 in our study, all the devices showed lower Voc values. These values (~1070 mV) are lower compared to those of the devices containing spiro-OMeTAD (~1100 mV) in spite of their deeper HOMO values (5.33 eV for V1305, 5.37 eV for V1306, and 5.46 for V1307 and V1308) compared to spiro-OMeTAD (5.00 eV).40 Therefore, the lower Voc values might be due to a contact issue at the perovskite/HTM interface producing higher charge recombination in comparison to spiro-OMeTAD-based devices. The fill factor (FF) is similar for devices containing spiro-OMeTAD, V1305, V1307, and V1308, but this main parameter differs for V1306-based devices, indicating poor film quality, which will negatively affect the hole charge extraction. The analysis of the film by top-view high-magnification SEM demonstrates the presence of pinholes in devices fabricated with V1306 (Figure S13a). The appearance of these pinholes is also observed in the device fabricated with V1308 (Figure S13b). However, for V1308, the efficiency is not affected, but it does affect the long-term device stability. The hysteretic behavior of the devices was estimated from the J–V curves collected by scanning the device from the forward bias (FB) to the short circuit (SC) followed by from SC to FB (Figure S14), and their PV parameters are reported in Table 2. The hysteresis index was calculated from the formulae previously reported,51 and values of 0.036, 0.100, 0.259, 0.047, and 0.037 were estimated for the devices containing spiro-OMeTAD, V1305, V1306, V1307, and V1308, respectively.

The stability of the unencapsulated devices was measured under 1 sun illumination and under a N2 atmosphere, as shown in Figure 3d. Devices containing V1305 and V1306 that have one and two enamine arms, respectively, are the most stable of the series and have a slightly better stability than devices that are composed of spiro-OMeTAD. However, the introduction of a second enamine moiety in the transconfigured V1308 induces a fastest decay and is completely detrimental for the stability, which is in good agreement with the inhomogeneity observed in the top-view SEM images, where the highest pinhole density was observed. Interestingly, a slight initial decay in PCE of the tetra-substituted V1307 device was observed in the beginning of the measurement during the first hour followed by the similar trend to V1305, V1306, and spiro-OMeTAD during the remaining time. Similar dynamic mechanisms have been observed, demonstrating that a quick degradation is activated by the migration of metal electrode particles through HTM, resulting in the contact with the perovskite layer.52,53 Stability measurements revealed that the number and position of enamine arms in the final HTM structure have a large impact on the stability of the final device.

### CONCLUSIONS

In conclusion, a new series of spirobifluorene-based hole-transporting enamines were synthesized and systematically studied. Novel HTMs are obtained by a simple and straightforward condensation reaction, which in contrast to spiro-OMeTAD, do not require expensive palladium catalysts.

| ID       | Voc (mV) | Jsc (mA cm^-2) | FF   | PCE (%) |
|----------|----------|----------------|------|---------|
| spiro-OMeTAD | REV | 1118 | 22.90 | 0.77 | 19.7 |
| V1305    | FWD | 1104 | 22.89 | 0.75 | 19.0 |
| V1306    | REV | 1077 | 23.17 | 0.76 | 19.0 |
| V1307    | FWD | 1043 | 23.15 | 0.71 | 17.1 |
| V1308    | REV | 1004 | 22.22 | 0.71 | 15.8 |
|          | FWD | 981  | 22.17 | 0.54 | 11.7 |
|          | REV | 1073 | 23.21 | 0.77 | 19.2 |
|          | FWD | 1052 | 23.18 | 0.75 | 18.3 |
|          | REV | 1074 | 23.44 | 0.76 | 19.1 |
|          | FWD | 1066 | 23.37 | 0.74 | 18.4 |

“REV, reverse bias; FWD, forward bias. Precondition: 2 s of light soaking. Illumination area through a shadow mask of 16 mm^2, a scan rate of 50 mV s^-1, and a voltage step of 10 mV.”
and inert conditions, and water is the only byproduct obtained. In addition, simple product workup and purification resulted in significantly reduced synthesis costs. The impact of the different number and substitution of enamine fragments was revealed through the optical, electrochemical, photophysical, and photovoltaic measurements. It was found that enamine fragments increase the glass-transition temperature of final HTMs that are more amorphous and morphologically stable. Moreover, synthesized enamine materials demonstrate a very high hole mobility and conductivity up to $9.4 \times 10^{-4}$ cm$^2$/Vs and $1.4 \times 10^{-3}$ S cm$^{-1}$, respectively. In summary, PSCs fabricated with the novel V1305 and V1307 HTMs present high-efficiency values exceeding 19%, with small hysteresis and stability being comparable to those of devices containing spiro-OMeTAD in the same testing period. This demonstrates that simple enamine condensation chemistry is a universal approach to obtain highly efficient and stable HTMs.

**METHODS**

**Device Fabrication.** Fluorine-doped tin oxide (FTO)-coated glass was laser scribed to avoid the direct contact between electrodes. The etched substrates were cleaned by the following procedure: 2% helmanex solution, deionized water, and ethanol were placed in an ultrasonic bath for 10 min and UV/O$_3$ treatment was performed for 15 min. Compact TiO$_2$ (c-TiO$_2$) (30 nm) was deposited by spray pyrolysis from titanium disopropoxide bis(acetylacetonate) (Sigma–Aldrich) in isopropanol solution (1:15, v/v) and annealed at 450 °C for 30 min. The mesoporous TiO$_2$ (m-TiO$_2$) layers were prepared from a TiO$_2$ paste (Dyesol 30 NR-D) solution (1 g in 9 mL of ethanol dilution) by spin-coating at 5000 rpm (1000 rpm/s acceleration, 15 s). The layer was sintered on a hot plate at 500 °C for 30 min. Following this, a 20 nm SnO$_2$ layer was prepared by dissolving SnCl$_4$ (Acros) in deionized water (12 μL in 988 μL of water) and spin-coated at 3000 rpm for 30 s (1000 rpm/s acceleration), followed by annealing at 190 °C for 1 h. The [(FAP-b$_1$)$_2$Cl$_2$(MAPbI$_3$)$_{2.5}$]$_{20}$ perovskite solution was prepared by mixing 17.41 mg of MABr, 27.02 mg of CsI, 57.06 mg of PbBr$_2$, 178.94 mg of FAI, and 548.60 mg of PbI$_2$, and it was dissolved in 1 mL of DMF/DMSO (0.78:0.22, v/v). Then, the perovskite solution was spin-coated at 2000 rpm for 10 s, followed by 5000 rpm for 30 s. During spinning in the second step, the antisolvent chlorobenzene (110 μL) was dropped on the sample 15 s before finishing the process. The films were annealed at 100 °C for 1 h inside the glovebox. Once the samples were cooled down, the HTM was deposited on top of the perovskite layer by spin-coating at 4000 rpm for 30 s. The spiro-OMeTAD was deposited from a 60 mM solution in chlorobenzene with tBP, tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) (FK209), and LiTFSI. The concentration of V-series HTMs was 20 mM. The molar ratio of additives for spiro-OMeTAD and each doped HTM solution was 0.5 for LiTFSI from a 1.8 M stock solution in acetonitrile and 3.3 for tBP and 0.03 for FK209 from a 0.25 M stock solution in acetonitrile. Finally, a 70 nm Au film was thermally evaporated as the top electrode. The cross-sectional film morphology was investigated by using a high-resolution SEM (Merlin, Zeiss) equipped with a GEMINI II column and a Schottky Field Emission gun. Images were acquired with an In-Lens Secondary Electron Detector at 3 kV.

**Thin Film and Device Characterization.** Conductivity measurements of V1305, V1306, V1307, V1308, and spiro-OMeTAD were carried out using the OFET configuration with a two-contact electrical conductivity setup. The OFET substrates were purchased from Fraunhofer IPMS. The substrates were first prepared with 20 min of oxygen plasma cleaning and subsequent film deposition of HTMs and spiro-OMeTAD by spin-coating following the same procedure as in the device fabrication, at 4000 rpm for 30 s from a chlorobenzene solution (20 mM) chemically doped with FK-209, LiTFSI, and tBP as additives. The conductivity measurements were carried out on the 2.5 μm channel by sweeping from –10 to 10 V (source–drain voltage) at a scan rate of 1 V s$^{-1}$ with a Keithley 2612A (Figure S8). The data were recorded using the KickStart software program. The channel width and height are 10 mm and 40 nm, respectively, and the gate capacity is 15 nF. The conductivity was calculated from a linear fit of the current–voltage measurement and Ohm’s law. The J–V characteristics were determined by using a 2400 Keithley system (scan rate: 50 mV s$^{-1}$ and 10 mV voltage step) in combination with a Xe-lamp Oriel sol3A sun simulator (Newport Corporation), previously calibrated to AM1.5G standard conditions by using the reference cell Oriel 91150 V. The devices were measured with 2 s of light soaking, and the illumination area was defined through a shadow mask of 16 mm$^2$. EQE was measured with an IQE200B quantum efficiency measurement system (Oriel, Newport, UK). The stability test was performed as maximum power tracking under 100 mW cm$^{-2}$ illumination with an LED power source. Note that during the stability test, the samples were placed in a measurement box purged continuously with nitrogen gas at 0% humidity to create an inert atmosphere. The box temperature was kept at 25 °C by a cooling system. A shadow mask of 16 mm$^2$ was used to define the illumination area during the long-term stability test. Top-view SEM images were recorded by an in-lens detector of the FEI Teneo Schottky field-emission SEM at a tension of 5 kV. The steady-state PL spectra of the glass/perovskite and glass/perovskite/HTM thin films were measured and recorded using a Fluorolog-3-22 spectrofluorometer. The spectra were recorded upon excitation at 625 nm with the sample illuminated from the front side (perovskite or the HTM side).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.1c01486.

Tables S1–S4 and Figures S1–S52; experimental section; detailed synthetic procedures; TGA data; DSC; optimized geometry of frontier molecular orbital diagrams; electronic absorption spectra; electronic excitation; V1305, V1306, V1307, and V1308 distributions; UV–vis/PL spectra of thin films; photoemission in air spectra; current–voltage measurements; $^1$H and $^{13}$C NMRs; MALDI-TOF-MS spectra; PESA; conductivity; SEM images; photovoltaic parameter statistics; J–V curves; EQE (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

Kaspars Rakstys — Department of Organic Chemistry, Kaunas University of Technology, Kaunas 50254, Lithuania; Email: kaspars.rakstys@ktu.lt

Vytautas Getautis — Department of Organic Chemistry, Kaunas University of Technology, Kaunas 50254, Lithuania; Email: vytautas.getautis@ktu.lt

Mohammad Khaja Nazeruddin — Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH-1951 Sion, Switzerland; Email: mdkhaja.nazeruddin@epfl.ch

**Authors**

Deimante Vaitukaityte — Department of Organic Chemistry, Kaunas University of Technology, Kaunas 50254, Lithuania

Cristina Momblona — Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH-1951 Sion, Switzerland; Email: mdkhaja.nazeruddin@epfl.ch

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Author Contributions
D.V. conducted the synthesis and structural characterization of the compounds and carried out UV–vis and PL measurements. C.M. and B.D. contributed to film preparation and device fabrication and testing. K.R. conceived the idea, K.R. and C.M. wrote the initial manuscript. C.I. contributed to the conductivity measurements and analysis. A.A.S. contributed to the SEM measurements and analysis. V.J. carried out the charge mobility measurements. A.G. performed computational simulations. T.M., A.M.A., and P.J.D. analyzed data. V.G. and M.K.N. supervised the research. All authors contributed to writing and reviewing this paper. This 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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