Macromolecules

Dopant-Free Hole-Transporting Polymers for Efficient and Stable Perovskite Solar Cells

Silvia Valero,[†] Silvia Collavini,[†] Sebastian F. Völker,[†] Michael Saliba,^{‡,§} Wolfgang R. Tress,[‡][®] Shaik M. Zakeeruddin,[‡] Michael Grätzel,^{*,‡®} and Juan Luis Delgado^{*,†,||}®

[†]POLYMAT University of the Basque Country UPV/EHU, Avenida de Tolosa 72, 20018 Donostia - San Sebastián, Spain [‡]Laboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

[§]Soft Matter Physics Group, Adolphe Merkle Institute, Chemin des Verdiers 4, CH-1700 Fribourg, Switzerland ^IIkerbasque, Basque Foundation for Science, 48013 Bilbao, Spain

S Supporting Information

ABSTRACT: A series of novel polymers (P1-P6) derived from the combination of different units (including thiophene, triarylamine, and spirobifluorene) were successfully synthesized, completely characterized, and used as hole-transporting materials (HTMs) for perovskite solar cells (PSCs). Solar cells with some of these materials as HTMs showed very good performances of almost 13% (12.75% for P4 and 12.38% for P6) even without additives, and devices based on these new HTMs show relatively improved stability against temperature compared to those based on PTAA. The presence of dopant



additives has been linked to long-term degradation, which is the main barrier to the large-scale commercialization of this innovative type of solar cell. Obtaining efficient PSCs without using dopants could represent a further step toward improvement of long-term stability and thus their introduction into the market.

INTRODUCTION

One of the most remarkable developments in the history of photovoltaics has been the emergence of perovskite solar cells. After their discovery in 2009, when Miyasaka et al. obtained 3.8% of efficiency using methylammonium lead iodide perovskite (MAPbI₃),¹ the performance of PSCs rose quickly to a certified record of 23.7%.² However, the fast growth in performance is not enough to guarantee a spot in the market of solar cells, which is still led by silicon solar cells.

As a matter of fact, despite their incredible performance advancement, PSCs still suffer from lack of long-term stability.^{3,4} Several adjustments have been attempted to obtain the desired long-term stable performance.⁵ In this effort, among others, hole-transporting materials (HTMs) have been intensively studied.⁶ Today, the best choice as HTM is still 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD), which is known and used in PSCs since 2012, when Snaith et al.⁷ and in parallel Grätzel et al.⁸ fabricated an all-solid device using this molecule as HTM. Nevertheless, spiro-OMeTAD is far from being the perfect HTM for different reasons: it has low conductivity and hole mobility, and to reach the best performances the use of dopants, such as lithium bis(trifuloromethanesulfonyl)imide (LiTFSI) and tert-butylpyridine (tBP), is required to improve its conductivity. These dopants are hygroscopic, and they might migrate into the perovskite layer during operation,

leading to losses in performance, although the mechanism is not yet clear.^{9,10} Also, higher temperatures are detrimental for this molecule, which crystallizes losing its efficiency as HTM.¹¹

Several other HTMs have been used to bypass the drawbacks of spiro-OMeTAD, both polymers and small molecules.^{12,13} Polymers have emerged as good candidates where the polymer poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) is one of the best known. The performances obtained with this HTM are highly comparable to spiro-OMeTAD.¹⁴ Even though PTAA showed improved stability at higher temperatures, it still requires dopants to achieve best performances, which is a problem for long-term stability. In addition to the aforementioned degradation mechanisms, the acetonitrile required to dissolve the dopant LiTFSI added to the HTM solution could partially corrode the underlying perovskite layer.

For all these reasons, the use of dopant-free HTMs could be a suitable strategy to get the required long-term stability. Working without dopants was already shown to be a feasible strategy, and there are few studies of dopant-free HTMs.⁶ Some small molecules have been tested recently as HTMs in PSCs in the absence of dopants; not only have they reached

Received: January 23, 2019 **Revised:** February 22, 2019



0R

OR









Figure 1. Chemical structures of monomers (M1-M5 and 2,7-dibromo-9,9'-spirobifluorene) and polymers (P1-P6).

efficiencies comparable to that of devices using doped *spiro*-OMeTAD, they also showed an improved stability.¹⁵⁻²⁴

With regard to polymers, they have been much less explored than small molecules even though they offer excellent properties, albeit most of them derive from previous OPVs and OLEDs. Recently, Park et al.²⁵ reported a novel polymeric HTM based on benzo[1,2-*b*:4,5:*b'*]dithiophene (BDT) and 2,1,3-benzothiadiazole (BT) units for using it in PSCs without using any dopant. A PCE of 17.3% was achieved, maintaining its initial efficiency for >1400 h. The same authors have reported a 19.8% on efficiency with a device fabricated with a donor–acceptor type dopant-free polymeric HTM. In their work the polymeric HTM, consisting of a BDT unit as a donor

and a BT unit as acceptor connected with a π -bridge, was incorporated in PSCs.²⁶

Also, in a work by Getautis, Saliba et al.²⁷ three new triarylamine-based polymers were tested as HTMs in the absence of dopants leading to a PCE of 12.3% with the polymer poly[3,5-dimethyl-N,N-diphenyl-4-(2-phenylprop-1-en-1-yl)aniline-4',4"-diyl], which was higher than that of PTAA (10.8%) measured under the same conditions. Moreover, devices prepared with this dopant-free polymer were stable for over 140 h without significant changes in the PCE, while devices with the doped polymer showed a significant decrease of efficiency already in the first few hours. Qiao et al.²⁸ reported the well-known polymer PDPP3T [poly[{2,5-

Scheme 1. Synthetic Route to Monomers M1-M5



bis(2-hexyldecyl)-2,3,5,6-tetrahydro-3,6-dioxopyrrolo[3,4-*c*]pyrrole-1,4-diyl}-*alt*-{[2,2':5',2"-terthiophene]-5,5"-diyl}] as dopant-free HTM in PSCs reaching a PCE of 12.3%, which was comparable with devices prepared with doped *spiro*-OMeTAD (12.34%) measured under the same conditions. In addition, PDPP3T-based PSC devices showed better stability in ambient air than doped *spiro*-OMeTAD. Neher, Stolterfoht, and co-workers have reported the highest efficiency with a device fabricated with a dopant-free polymeric HTM. They employed PTAA as dopant-free HTM in inverted PSCs reaching a 20.4% on efficiency and approaching the fill factor Shockley–Queisser limit.²⁹

All these results indicate the possibility of using polymers as dopant-free HTMs for the development and commercialization of stable PSCs avoiding the use of additives.

Herein, a series of new conjugated polymers (P1-P6) containing different well-known hole-accepting units in the

backbone such as thiophene, triarylamine, and spirobifluorene³⁰ were successfully synthesized via Suzuki or Yamamoto polymerization. The optical and electrochemical properties, as well as the molecular weights and thermal properties of all polymers, were investigated. The new polymers P1-P6 were incorporated into PSCs to evaluate their performance as HTMs. Moreover, the heating resistance of the champion devices based on polymers P4 and P6 was tested.

RESULTS AND DISCUSSION

Synthesis. The chemical structures of the synthesized polymers **P1–P6** and the necessary monomers for preparation are displayed in Figure 1.

The design of the six new polymers was inspired by *spiro*-OMeTAD and PTAA, the latter being the only polymeric HTM that could work as efficiently as spiro-type small molecules.³¹ Polymers **P1** and **P2** are composed of a



spirobifluorene unit in combination with two different donor moieties, a thiophene and a triarylamine derivative, which are known to possess high hole-transporting and electron-blocking ability. Moreover, to ensure sufficiently high solubility for device fabrication and good film formation, branched alkyl chains (2-ethylhexyl) were introduced in key positions of those donor units.

In polymers P3-P6, the possibility to introduce more donor groups in the backbone of the polymers was explored to modulate the HOMO energy level of the polymers for a better hole transport from the perovskite to the HTM. Therefore, we designed polymers P3-P6, each one containing triphenylamine extended units in combination with different donor systems as thiophene (P3), spirobifluorene (P4), or triarylamine (P5) units. As in polymers P1 and P2, polymers P3–P6 will benefit from the enhanced solubility given by the introduction of alkyl groups.

The procedure for the synthesis of monomers M1-M5 is shown in Scheme 1, while the complete experimental details can be found in the Supporting Information. Monomer M2was synthesized and purified according to published procedures,³²⁻³⁵ while M1 was synthesized in two steps. First, the Kumada coupling of 3,4-dibromothiophene with 2-



Figure 2. (A) ¹H NMR spectrum and (B) MALDI-TOF of polymer P2.

ethylhexyl bromide provided thiophene 1, which after Ircatalyzed borylation afforded M1.

The syntheses of monomers M4 and M5 were performed following literature procedures.^{36–38} The synthesis of M3 started with the reaction between 4-bromophenylamine with an excess of 1-[(2-ethylhexyloxy]-4-iodobenzene (2) to give 4bromo-*N*,*N*-bis[4-(2-ethylhexyloxy)phenyl)aniline (5). After that, Buchwald–Hartwig reaction of compound 5 with diphenylamine gave *super*-triarylamine 6, which finally reacted with an excess of NBS yielding the monomer M3 (Scheme 1).

The six new polymers P1-P6 were then synthesized recurring to either Suzuki (P1-P5) or Yamamoto (P6) coupling polymerization. Pd-catalyzed Suzuki polymerization of the diboronic ester monomers **M1** and **M2** with 2,7dibromo-9,9'-spirobifluorene yielded **P1** and **P2**, respectively, using sodium bicarbonate as base and toluene as solvent. Following the same procedure, polymers **P3**, **P4**, and **P5** were synthesized by reaction of the corresponding monomers **M1**, **M4**, and **M5** with the *super*-triarylamine **M3**, respectively. Homopolymer **P6** was synthesized through Ni-mediated Yamamoto polymerization of **M3** in the presence of 1,5cyclooctadiene (COD) and 2,2'-bipyridine in a solvent mixture of DMF and toluene (1:1) (Scheme 2).

The resulting polymers were purified from the residual catalyst and low molecular weight impurities by precipitation in MeOH (P1-P5) or MeOH:HCl (P6) and subsequent

extraction with different solvents through Soxhlet extraction. This processes yielded polymers in good (P1, P2, P4–P6) or moderate (P3) yields. All polymers show good solubility in common organic solvents, such as dichloromethane, chloroform, THF, or toluene.

The composition and chemical structure of all polymers were confirmed by ¹H NMR and MALDI-TOF spectrometry (see Figure 2 and Figures S14–S24). In the latter, peaks corresponding to the building blocks were clearly visible.

The size of the polymers was estimated by size exclusion chromatography (SEC) in THF with polystyrene standards for calibration, and the data are found in Table 1. The longest molecular chain was registered for polymer **P1**, with a number-average molecular weight (M_n) of 9651 g mol⁻¹, leading to a

Table 1. Molecular Weights and Thermal Properties of Polymers P1–P6

	$M_{\rm p}$	M_{w}				
polymer	$(g m ol^{-1})$	$(g mol^{-1})$	$X_{\rm n}$	PDI	$T_{\rm d}$ (°C)	T_{g} (°C)
P1	9651	21635	15.5	2.24	302.57	147.8
P2	5551	11390	8.08	2.05	371.74	241.8
P3	3209	4746	3.30	1.48	327.14	76.50
P4	4403	10528	4.48	2.39	392.03	198.1
P5	4681	8663	4.98	1.85	390.62	141.5
P6	5812	12443	8.71	2.14	390.66	103.9

degree of polymerization (X_n) of 16. The corresponding weight-average molecular weight (M_w) of polymer **P1** was 21635 g mol⁻¹, showing a relatively small polydispersity (PDI = M_w/M_n) of 2.24. Molecular weights of polymers **P2–P6** showed a comparable M_n in the 5812–3209 g mol⁻¹ range and a M_w ranging from 4746 to 12443 g mol⁻¹ with a PDI in the range 1.48–2.39.

Thermal Properties. Thermogravimetric analysis performed at a heating rate of 10 $^{\circ}$ C/min under a nitrogen atmosphere indicated the high thermal stability of copolymers P1-P5 and homopolymer P6 (Figure 3A), showing



Figure 3. (A) Thermogravimetric heating curves of polymers P1-P6 (heating rate 10 °C/min). (B) Differential scanning calorimetry second heating curves for polymers P1-P6 (heating rate 20 °C/min).

decomposition temperatures (T_d) (2% weight loss) ranging from 303 to 392 °C (Table 1), which is well above operational conditions. All polymers exhibit weight loss before decomposition, which may be attributed to the loss of solvent traces.

Differential scanning calorimetry (DSC) measurements of the investigated polymers P1–P6 reveal that all of them are fully amorphous (Figure 3B and Table 1). DSC measurements show that the glass transition temperature (T_g) of polymers P1, P2, P4, and P5 are at 147.8, 241.8, 198.08, and 141.53 °C, respectively, which are higher than that of *spiro*-OMeTAD (125 °C),³⁹ indicating a more stable amorphous state. The T_g of polymer P6 was determined to be 103.85 °C, whereas the additional thiophene unit in polymer P3 significantly influences the T_{g} lowering it to 76.5 °C.

Optical Properties. The normalized UV-vis absorption spectra of copolymers P1-P6 in dichloromethane are depicted in Figure 4A. Absorption peaks of all polymers are located in the UV region, and there is no significant absorption in the visible region, which is necessary for not competing with the perovskite in the absorption of light.¹² Upon comparison of the absorption of the spirobifluorene-based copolymers P1 and P2, the latter presents a maximum absorption peak at 376 nm, which is shifted toward the red region compared to P1 (358 nm), due to a larger π -conjugated system, mostly owing to the



Figure 4. (A) Normalized UV–vis spectra of P1–P6 in DCM at concentrations of 3.03×10^{-5} , 2.71×10^{-5} , 2.51×10^{-5} , 2.49×10^{-5} , 2.21×10^{-5} , and 3.27×10^{-5} mol L⁻¹, respectively. (B) Normalized fluorescence spectra of polymers P1–P6 in DCM.

presence of three additional phenyl rings in P2. This is also the reason why copolymer P2 presents a higher molar absorption coefficient (ε) than polymer P1.

As for polymers bearing the triphenylamine extended unit **P3–P6**, they showed maximum absorption wavelengths in between 350 and 380 nm. As the amount of delocalization in the polymer increases, there is less energy gap between π and π^* orbitals, and a higher wavelength is necessary for absorption. Therefore, polymers **P3** and **P6** present the lowest maximum absorption wavelength (348 and 349 nm, respectively) while polymers **P4** and **P5**, with more phenyl rings in their backbone, which implies more delocalization, have maximum absorption at 383 and 365 nm, respectively.

From the onset of the absorption edge in the longer wavelength region, the optical band gap (E_g) was estimated, and the values are reported in Table 2. In addition, the photoluminescence spectra (Figure 4B) showed emission peaks at 451, 424, 510, 549, 494, and 491 nm for polymers **P1–P6**, respectively.

Electrochemical Properties. The electrochemical properties of the polymers were investigated by cyclic voltammetry (CV) measured in a 0.1 M solution of nBu_4NPF_6 in anhydrous DCM. Their HOMO energy levels (E_{HOMO}) were obtained from the onset of the first oxidation (E_{onset}^{Ox1}) during CV measurements using the ferrocene/ferrocinium (Fc/Fc⁺) redox couple as the internal standard. The highest occupied molecular orbital (HOMO) level is calculated according to the equation E_{HOMO} (eV) = $-4.8 - E_{onset}^{Ox1}$ and the data are listed in Table 2.

Polymer **P2** exhibits one reversible oxidation process at a $E_{1/2}^{Ox1}$ value of 0.31 V vs Fc/Fc⁺, indicating its electrochemical stability, while polymer **P1** shows a poorly reversible oxidation wave at E_{onset}^{Ox1} value of 0.61 V vs Fc/Fc⁺ (Figure 5A). Comparing the electrochemical data, we could find that **P2** was more easily oxidized than **P1**. The HOMO energy levels

Table 2. Optical and Electrochemical Properties of Polymers P1-P6

polymer	λ_{abs} (nm)	$\lambda_{\rm fl}~({\rm nm})$	$\varepsilon ~(\mathrm{M^{-1}~cm^{-1}})$	$E_{1/2}^{\rm Ox1}$ (V)	$E_{\text{onset}}^{\text{Ox1}}$ (V)	$E_{\rm LUMO}~({\rm eV})$	$E_{\rm HOMO}~({\rm eV})$	$E_{\rm g}~({\rm eV})$
P1	358	451	27055		0.61	-2.33	-5.41	3.08
P2	376	424	32284	0.31	0.21	-2.04	-5.01	2.97
P3	348	510	33982	0.01	-0.07	-1.61	-4.73	3.12
P4	383	549	40399	-0.01	-0.09	-1.81	-4.71	2.90
P5	369	494	45329	-0.03	-0.10	-1.65	-4.70	3.05
P6	349	491	26586	-0.02	-0.12	-1.63	-4.68	3.05



Figure 5. Cyclic voltammograms of (A) polymers P1 and P2 and (B) polymers P3–P6 in DCM/nBu_4NPF_6 (0.1 M) at a scan rate 250 mV s⁻¹. (C) Energetic levels of polymers P1–P6 and perovskite light absorber layer used in this study.



Figure 6. Statistical deviation of the photovoltaic parameters for PSCs using polymers P1-P6 and PTAA as HTMs.

 $(E_{\rm HOMO})$ of **P1** and **P2** calculated from CV are -5.41 and -5.01 eV, respectively. The reported HOMO energy level for the triple cation perovskite, used in this work, is -5.45 eV,⁴⁰ revealing the favorable hole transfer from the perovskite to the HTMs (Figure 5C). Moreover, the lowest unoccupied molecular orbital energy levels ($E_{\rm LUMO}$) were estimated from the difference between $E_{\rm HOMO}$ and $E_{\rm g}$ derived from UV-vis spectroscopy of the polymers as -2.33 and -2.04 eV for **P1** and **P2**, respectively. Because of the $E_{\rm g}$ and the high $E_{\rm LUMO}$, the compounds are suitable not only for hole transfer but also to block electrons.

As in polymers P1 and P2, the voltammograms of polymers P3-P6 show only oxidation processes, while no reduction processes were observed in the operation window of the solvent-electrolyte (Figure 5B). Polymers P3, P4, and P6 showed two reversible oxidations waves, while polymer P5 showed three reversible oxidations. The strong electron donor properties of the additional diaryalmine substituents in polymers P3-P6 compared to polymers P1 and P2 are reflected at the remarkably low first oxidation potentials at $E_{1/2}^{\text{Ox1}}$ values of 0.01, -0.01, -0.03, and -0.02 V vs Fc/Fc⁺ for P3, P4, P5, and P6, respectively. According to the similar redox potentials, also the HOMO energy levels of polymers P3-P6 are nearly identical, with values around 4.7 eV. With this values, polymers P3-P6 could be suitable for efficient hole transfer from the perovskite to the HTM, similarly to polymers P1 and P2. The LUMO energy levels of polymers P3-P6 lie between -1.61 and -1.81 eV, as shown in Table 2.

Photovoltaic Performance of Devices. To evaluate their behavior as hole-transport materials, the new polymers were incorporated without any doping additives in regular mesoporous PSCs. Polymer PTAA was used as HTM for reference devices without additives as well.

The best performances obtained so far with the use of the most common polymeric HTM (PTAA) are achieved by doping the HTM solution with both *tert*-butylpyridine (*tBP*) and bis(trifluoromethane)sulfonimide lithium salt (LiTFSI).¹⁴ These dopants, in fact, help enhance the performances of the HTM with mechanisms that are not yet completely clear.

The perovskite used for this study contains three different organic cations (cesium, methylammonium, and formamidinium).⁴⁰ The device structure is the following: fluorine-doped tin oxide (FTO)/compact TiO₂/mesoporous TiO₂/ $Cs_x(MA_{0.17}FA_{0.83})_{(100-x)}Pb(_{10.83}Br_{0.17})_3/HTM/Au$. The detailed fabrication procedure can be found in the Supporting Information.

Figure 6 shows the photovoltaic parameters of the solar cell devices containing the polymers P1–P6, while Table 3 shows the highest value obtained with the several polymers. I-V curves of the best cells can be found in the Supporting Information.

Unexpectedly, thiophene-containing polymers P1 and P3 gave very bad efficiencies. The most affected parameters are $V_{\rm OC}$ and especially FF, the latter being an indicator of a low conductivity of the material. I-V curves of these polymers show an S-shape (Figure S25), which is a symptom of bad charge extraction at the hole-transporting layer and also leads to low $V_{\rm OC}$. This is usually due to a high energy barrier between the HOMO of perovskite and of the HTM, but since this is not the case, a low conductivity could explain this behavior. This is confirmed by studies of series resistance of the devices (Figure 7). The series resistance is extracted from the I-V curves measured under 1 sun in a backward scan.

Table 3. Photovoltaic Parameters Determined from J-VMeasurements Using Polymers P1–P6 and PTAA as HTMs

HTM	$V_{\rm OC}$ (V)	$J_{\rm SC}~({\rm mA~cm^{-2}})$	FF (%)	PCE (%)	$R_{\rm s} \left(\Omega \right)$
PTAA	1.093	21.1	68	15.8	47.2
P1	0.690	12.0	26	2.2	481.1
P2	1.037	15.9	60	9.8	76.6
P3	0.818	15.6	34	4.3	141.1
P4	1.094	18.5	63	12.7	41.0
P5	0.972	15.3	50	7.5	103.5
P6	1.031	20.7	72	12.4	28.7



Figure 7. Series resistance of several devices containing polymers P1– P6 compared with PTAA.

Here, an upper limit of R_s is approximated by finding the minimum of the inverse differential slope of the I-V curve in forward direction (between 1.1 and 1.2 V). Thus, the series resistance value is linked to the FF value. The incorporation of side alkyl chains into the polymer structure is an efficient way to improve the solubility of the polymers; however, these alkyl chains constitute an insulating part within the polymer. In the case of polymers P1-P6, all of them possess alkyl chains in their structure. It is clearly visible that polymers P1 and P3, which give the lowest efficiency, have the highest series resistance (Figure 7 and Table 3). Interestingly, both of them have a thiophene unit in their backbone, in which two alkyl chains are attached to the thiophene ring. Additionally, polymer P3 has two more additional alkyl chains attached to the triaryalmine extended unit, but the presence of more side alkyl chains did not lead to higher R_s compared to the P1based device. In comparison to P1 and P3, polymers P2 and **P5** lead to perovskite devices with much lower $R_{\rm e}$. In this case, polymer P5 has two alkyl chains attached to the triarylamine extended unit while polymer P2 only has one alkyl chain in the p-position of the triarylamine unit. Finally, polymers P4 and P6, which contain two alkyl chains per unit, lead to devices with the lowest R_s, even lower than PTAA-based devices. Taking into account that PTAA does not contain any alkyl chain, it could be concluded that in this case the conductivity of the layers is not affected by the presence of insulating alkyl chains. In fact, apart from helping the material to get better solution processability, side chains also strongly affect film microstructures, which could also affect the conductivity of the layer.41

Apart from P1- and P3-based devices, the rest of the polymers show very good efficiencies, which in the case of P4 and P6 are highly comparable to those of PTAA, used as reference. The PCEs of 12.75% and 12.38% for polymer P4 and P6, respectively, are remarkable, in particular considering

that a further optimization might lead to even higher values. With regard to P4, the V_{OC} of the devices containing this polymer exceeded that of PTAA for several devices. The slightly lower FF, which is correlated to a lower conductivity, is the major cause of the lower PCE. P6, on the contrary, presents astonishing FF, but both J_{SC} and V_{OC} are slightly lower than those of PTAA, maybe due to higher interface recombination because the conductivity of P6 seems to be higher than that of PTAA, according to the series resistance values (Figure 7). Last, P2 and P5 give efficiencies a bit lower than the previous structures due to a low J_{SC} .

A cross section of the devices containing P6 can be seen in Figure 8. The HTM layer can barely be seen, since it is very thin (\sim 20 nm). The concentration of the polymer solution is 7 mg/mL, while PTAA is deposited from a 10 mg/mL solution.



Figure 8. Cross-sectional SEM images of a device with P6.

The best devices, using polymers P4 and P6, underwent a simple high-temperature stability test to evaluate their resistance to this kind of stress in comparison with PTAA. As mentioned before, sensitivity to high temperatures is one of the drawbacks of the most used HTM, *spiro*-OMeTAD. The cells' performances were measured before and after being heated for 12 h at 65 °C in nitrogen atmosphere. The performances given by the novel polymers are better than those of PTAA after the stress test (Figure 9).



Figure 9. Normalized PCE for champion devices prepared with PTAA, P4, and P6 as HTMs.

EXPERIMENTAL SECTION

Synthesis of P1. 2,2'-(3,4-Bis(2-ethylhexyl)thiophene-2,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (M1, 368 mg, 657 μ mol) was put in a Schlenk flask under nitrogen. Next, anhydrous toluene (16 mL) and aqueous 0.2 M NaHCO₃ (5.98 mL, 1.20 mmol) were injected together with 2,7-dibromo-9,9"-spirobifluorene (312 mg, 657 μ mol) and Aliquat 336 (56.8 mg) under a nitrogen atmosphere. The

reaction mixture was degassed by bubbling nitrogen for 30 min before and after $Pd(PPh_3)_4$ (11.4 mg, 9.86 μ mol) was added, and the mixture was stirred vigorously and refluxed for 135 h. Afterward, 30 mL of CHCl₃ and 30 mL of water were added, and upon separation of the phases, the organic phase was washed with 50 mL of brine. Next, the solvent was removed under reduced pressure, and the resulting residue was dissolved in 4 mL of CHCl₃ and dripped into 150 mL of cold MeOH. The green precipitate was filtered off and washed consecutively with MeOH (3 days), hexane (7 days), and acetone (1 day) using a Soxhlet extractor. Each washing lasted until no residue could be found in the chosen solvent (319 mg, 77%). SEC: $M_{\rm p}$ = 9651, M_w = 21635, PDI = 2.2. MS (MALDI-TOF, DCTB): calculated for C45H48S [M⁺]: 620,347, found: building blocks. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.87-7.70 (4H), 7.40-7.24 (4H), 7.12-6.99 (2H), 6.77-6.65 (4H), 2.42-2.14 (4H), 1.22-1.10 (2H), 1.10-0.78 (16H), 0.76-0.65 (6H), 0.51-0.36 (6H).

Synthesis of P2. 4-(2-Ethylhexyloxy)-N,N-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)aniline (M2, 358 mg, 571 μ mol) was put in a Schlenk flask under nitrogen. Next, anhydrous toluene (14 mL) and aqueous 0.2 M NaHCO₃ (5.20 mL, 1.04 mmol) were injected together with 2,7-dibromo-9,9"-spirobifluorene (271 mg, 571 μ mol) and Aliquat 336 (60.9 mg) under a nitrogen atmosphere. The reaction mixture was purged with nitrogen for 30 min before and after $Pd(PPh_3)_4$ (9.90 mg, 8.57 μ mol) was added. The mixture was stirred vigorously and refluxed for 135 h, and 30 mL of CHCl₃ and 30 mL of water were added afterward. The phases were separated; the aqueous phase was extracted with $CHCl_3$ (1 \times 30 mL), and the combined organic phases were washed with 50 mL of brine, dried over anhydrous Na2SO4, and concentrated under reduced pressure. The residue was dissolved in 4 mL of CHCl₃ and dripped into 150 mL of cold MeOH. The green precipitate was filtered off and washed consecutively with MeOH (3 days), hexane (4 days), and acetone (2 days) using a Soxhlet extractor. Each washing lasted until no residue could be found in the chosen solvent (322 mg, 82%). SEC: M_n = 5551, M_w = 11390, PDI = 2.1. MS (MALDI-TOF, DCTB): calculated for C₅₁H₄₃NO [M ⁺]: 685.322, found: building blocks.¹H NMR (300 MHz, CD_2Cl_2), δ (ppm): 7.99–7.76 (4H), 7.66–7.48 (2H), 7.48-7.02 (16H), 6.95-6.67 (4H), 3.86-3.71 (2H), 1.77-1.62 (1 H), 1.56-1.22 (8H), 1.01-0.80 (6H).

Synthesis of P3. The dibrominated compound M3 (446 mg, 539 μ mol) was put in a Schlenk flask under nitrogen. Next, anhydrous toluene (13 mL) and aqueous 0.2 M NaHCO₃ (4.90 mL, 981 μ mol) were injected together with 2,2'-(3,4-bis(2-ethylhexyl)thiophene-2,5diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (M1, 301 mg, 539 μ mol) and Aliquat 336 (45.0 mg) under a nitrogen atmosphere. The reaction mixture was purged with nitrogen for 30 min before and after Pd (PPh₃)₄ (9.34 mg, 8.09 μ mol) was added. The mixture was stirred vigorously and refluxed for 135 h, and 30 mL of DCM and 30 mL of water were added afterward. The aqueous phase was extracted with DCM (1×30 mL), and the combined organic phases were washed with 50 mL of brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was dissolved in 4 mL of DCM and dripped into 150 mL of cold MeOH. The green precipitate was filtered off and washed consecutively with MeOH (4 days), CH₃CN (2 days), and acetone (7 days) using a Soxhlet extractor. Each washing lasted until no residue could be found in the chosen solvent. SEC: $M_n = 3209$, $M_w = 4746$, PDI = 1.5. MS (MALDI-TOF, DITHRANOL): calculated for C₆₆H₈₈N₂O₂S [M⁺]: 972.656, found building blocks.¹H NMR (300 MHz, CD_2Cl_2), δ (ppm): 7.52–6.78 (20H), 3.86-3.77 (4H), 2.69-2.56 (4H), 179-1.64 (2H), 1.57-1.03 (34H), 0.99-0.64 (24H).

Synthesis of P4. The dibrominated compound **M3** (345 g, 417 μ mol) was put in a Schlenk flask under nitrogen. Next, anhydrous toluene (10 mL) and aqueous 0.2 M NaHCO₃ (3.79 mL, 758 μ mol) were injected together with 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-spirobi[fluorene] (**M4**, 237 mg, 417 μ mol) and Aliquat 336 (35.0 mg) under a nitrogen atmosphere. The reaction mixture was purged with nitrogen for 30 min before and after Pd (PPh₃)₄ (7.72 mg, 6.25 μ mol) was added. The mixture was stirred vigorously and refluxed for 135 h. Afterward, 30 mL of DCM and 30

mL of water were added, and the phases were separated. The aqueous phase was extracted with DCM (1 × 30 mL), and the combined organic phases were washed with 50 mL of brine, dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was dissolved in 4 mL of DCM and dripped into 150 mL of cold MeOH. The green precipitate was filtered off and washed consecutively with MeOH (5 days), hexane (2 days), and acetone (4 days) using a Soxhlet extractor. Each washing lasted until no residue could be found in the chosen solvent (276 mg, 67%). SEC: M_n = 4403, M_w = 10528, PDI = 2.4. MS (MALDI-TOF, DCTB): calculated for C₇₁H₆₈N₂O₂[M ⁺]: 980.527, found: building blocks. ¹H NMR (300 MHz, CD₂Cl₂), δ (ppm): 8.04–6.68 (34H), 3.87–3.74 (4H), 178–1.65 (2H), 1.55–1.25 (16H), 1.01–0.81 (12H).

Synthesis of P5. The dibrominated compound M3 (306 mg, 370 μ mol) was put in a Schlenk flask under nitrogen. Next, anhydrous toluene (9 mL) and aqueou 0.2 M NaHCO₃ (3.37 mL, 673 µmol) were injected together with 4-bromo-N-(4-bromophenyl)-N-(4methoxyphenyl)aniline (M5, 231 mg, 370 µmol) and Aliquat 336 (47.8 mg) under a nitrogen atmosphere. The reaction mixture was purged with argon for 30 min before and after Pd (PPh₃)₄ (6.42 mg, 5.55 μ mol) was added. The mixture was stirred vigorously and refluxed for 4 days, and 30 mL of DCM and 30 mL of water were added afterward. The aqueous phase was extracted with 30 mL of DCM, and the combined organic phases were washed with 50 mL of brine, dried over anhydrous Na2SO4, and concentrated under reduced pressure. The residue was dissolved in 4 mL of DCM and dripped into 150 mL of cold MeOH. The brown precipitate was collected by filtration and washed consecutively with MeOH (3 days), acetone (2 days), hexane (2 days), and MeOH (3 days) using a Soxhlet extractor. Each washing lasted until no residue could be found in the chosen solvent (176 mg, 46%). SEC: $M_p = 4681$, $M_w = 8663$, PDI = 1.9. MS (MALDI-TOF, HCCA): calculated for C₆₅H₆₉N₃O₃ [M ⁺]: 939.533, found: building blocks. ¹H NMR (300 MHz, CD_2Cl_2), δ (ppm): 7.66-6.64 (32H), 3.89-3.66 (7H), 179-1.61 (2H), 1.58-1.21 (16H), 1.01–0.77 (12H).

Synthesis of P6. A mixture of Ni (COD)₂ (375 mg, 1.36 mmol), 2,2'-bipyridine (213 mg, 1.36 mmol), 1,5-cyclooctadiene (167 µL, 1.36 mmol), degassed anhydrous toluene (3 mL), and degassed anhydrous dimethylformamide (3 mL) was stirred at room temperature under a nitrogen atmosphere for 30 min. A solution of compound M3 (470 mg, 568 μ mol) in degassed anhydrous toluene (9.5 mL) and degassed anhydrous dimethylformamide (9.5 mL) was added, and the mixture was stirred at 65 °C for 7 days. The reaction mixture was poured into MeOH/HCl (20%) (4:1, 500 mL) and stirred for 30 min. The green precipitate was filtered off and washed consecutively with MeOH (6 days), acetone (2 days), and CH₃CN (3 days) using a Soxhlet extractor. Each washing lasted until no residue could be found in the chosen solvent (194 mg, 51%). SEC: $M_n =$ 5812, M_w = 12443, PDI = 2.1. MS (MALDI-TOF, DCTB): calculated for C46H54N2O2 [M +]: 666,417, found: building blocks. ¹H NMR (300 MHz, (CD₂Cl₂), δ (ppm): 7.54–7.30 (4H), 7.18–6.70 (16H), 3.93-3.73 (4H), 178-1.62 (2H), 1.57-1.21 (16H), 1.01-0.81 (12H).

CONCLUSIONS

Several polymeric materials based on thiophene, triarylamine, or spirobifluorene units have been successfully synthesized, characterized, and incorporated into PSCs as HTMs. Novel HTMs exhibit excellent thermal and optoelectronics properties, and they present suitable HOMO levels which are perfectly aligned with that of the perovskite used in this study. PSCs based on dopant-free P4 and P6 as the HTM afford an impressive PCE of 12.75% and 12.38%, which are comparable to that of that obtained employing the well-known PTAA. In addition, we demonstrated that devices based on P4 and P6 showed higher thermal stability than devices based on PTAA most likely because both polymers present high thermal stability.

However, further investigation is required to dig deeper into the possible advantages that these polymers could give, since devices were not optimized and more in-depth investigations regarding stability are required. The investigation of new possible structures as charge transport materials is fundamental to reach the best cell possible to open up a space for PSCs in the market, and the possibility of working without additives is undoubtedly an important step.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.9b00165.

General methods and materials, construction and testing of the perovskite solar cells, synthesis and characterization of monomers M1–M5, intermediates 1–8, ¹H NMR spectra of polymers P1–P6, monomers M1–M5, intermediates 1–8, MALDI-TOF of polymers P1–P6, I-V curves of devices (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: juanluis.delgado@polymat.eu. *E-mail: michael.graetzel@epfl.ch.

ORCID [©]

Wolfgang R. Tress: 0000-0002-4010-239X Michael Grätzel: 0000-0002-0068-0195 Juan Luis Delgado: 0000-0002-6948-8062

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

S.V. acknowledges Polymat Foundation for a PhD research position. S.C. acknowledges Basque Government for a PREDOC grant. J.L.D. acknowledges Ikerbasque, the Basque Foundation for Science, for an "Ikerbasque Research Fellow" contract, Polymat Foundation and MINECO of Spain for CTQ 2016-81911-REDT grant, and Iberdrola Foundation for financial support.

ABBREVIATIONS

AcOEt, ethyl acetate; DCM, dichloromethane; PE, petroleum ether; THF, tetrahydrofuran.

REFERENCES

(1) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *J. Am. Chem. Soc.* **2009**, *131* (17), 6050–6051.

(2) National Renewable Energy Laboratory. Best Research-Cell Efficiencies. 2018, 2020.

(3) Kim, G. W.; Kang, G.; Malekshahi Byranvand, M.; Lee, G. Y.; Park, T. Gradated Mixed Hole Transport Layer in a Perovskite Solar Cell: Improving Moisture Stability and Efficiency. *ACS Appl. Mater. Interfaces* **2017**, *9* (33), 27720–27726.

(4) Salhi, B.; Wudil, Y. S.; Hossain, M. K.; Al-Ahmed, A.; Al-Sulaiman, F. A. Review of Recent Developments and Persistent Challenges in Stability of Perovskite Solar Cells. *Renewable Sustainable Energy Rev.* **2018**, *90* (March), 210–222.

(5) Niu, G.; Guo, X.; Wang, L. Review of Recent Progress in Chemical Stability of Perovskite Solar Cells. J. Mater. Chem. A 2015, 3 (17), 8970–8980.

(6) Rezaee, E.; Liu, X.; Hu, Q.; Dong, L.; Chen, Q.; Pan, J.; Xu, Z. Dopant-Free Hole Transporting Materials for Perovskite Solar Cells. *Sol. RRL* **2018**, *2*, 1800200.

(7) Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J. Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites. *Science (Washington, DC, U. S.)* **2012**, 338 (6107), 643–647.

(8) Kim, H. S.; Lee, C. R.; Im, J. H.; Lee, K. B.; Moehl, T.; Marchioro, A.; Moon, S. J.; Humphry-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*, 1–7.

(9) Bailie, C. D.; Unger, E. L.; Zakeeruddin, S. M.; Grätzel, M.; McGehee, M. D. Melt-Infiltration of Spiro-OMeTAD and Thermal Instability of Solid-State Dye-Sensitized Solar Cells. *Phys. Chem. Chem. Phys.* **2014**, *16* (10), 4864.

(10) Hawash, Z.; Ono, L. K.; Raga, S. R.; Lee, M. V.; Qi, Y. Air-Exposure Induced Dopant Redistribution and Energy Level Shifts in Spin-Coated Spiro-MeOTAD Films. *Chem. Mater.* **2015**, *27* (2), 562–569.

(11) Malinauskas, T.; Tomkute-Luksiene, D.; Sens, R.; Daskeviciene, M.; Send, R.; Wonneberger, H.; Jankauskas, V.; Bruder, I.; Getautis, V. Enhancing Thermal Stability and Lifetime of Solid-State Dye-Sensitized Solar Cells via Molecular Engineering of the Hole-Transporting Material Spiro-OMeTAD. ACS Appl. Mater. Interfaces **2015**, 7 (21), 11107–11116.

(12) Völker, S. F.; Collavini, S.; Delgado, J. L. Organic Charge Carriers for Perovskite Solar Cells. *ChemSusChem* **2015**, *8* (18), 3012–3028.

(13) Marinova, N.; Valero, S.; Delgado, J. L. Organic and Perovskite Solar Cells: Working Principles, Materials and Interfaces. *J. Colloid Interface Sci.* **201**7, 488, 373–389.

(14) Yang, W. S.; Noh, J. H.; Jeon, N. J.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I. High-Performance Photovoltaic Perovskite Layers Fabricated through Intramolecular Exchange. *Science (Washington, DC, U. S.)* **2015**, 348 (6240), 1234–1237.

(15) 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 C3h Symmetrical Truxene Core for Highly Efficient Perovskite Solar Cells. *J. Am. Chem. Soc.* **2016**, *138* (8), 2528–2531.

(16) Paek, S.; Qin, P.; Lee, Y.; Cho, K. T.; Gao, P.; Grancini, G.; Oveisi, E.; Gratia, P.; Rakstys, K.; Al-Muhtaseb, S. A.; et al. Dopant-Free Hole-Transporting Materials for Stable and Efficient Perovskite Solar Cells. *Adv. Mater.* **2017**, *29*, 1606555.

(17) Zhang, F.; Zhao, X.; Yi, C.; Bi, D.; Bi, X.; Wei, P.; Liu, X.; Wang, S.; Li, X.; Zakeeruddin, S. M.; Grätzel, M. Dopant-Free Star-Shaped Hole-Transport Materials for Efficient and Stable Perovskite Solar Cells. *Dyes Pigm.* **2017**, *136*, 273–277.

(18) Rakstys, K.; Paek, S.; Gao, P.; Gratia, P.; Marszalek, T.; Grancini, G.; Cho, K. T.; Genevicius, K.; Jankauskas, V.; Pisula, W.; Nazeeruddin, M. K. Molecular Engineering of Face-on Oriented Dopant-Free Hole Transporting Material for Perovskite Solar Cells with 19% PCE. J. Mater. Chem. A **2017**, 5 (17), 7811–7815.

(19) Sun, M.; Liu, X.; Zhang, F.; Liu, H.; Liu, X.; Wang, S.; Xiao, Y.; Li, D.; Meng, Q.; Li, X. Simple Dopant-Free Hole-Transporting Materials with p- π Conjugated Structure for Stable Perovskite Solar Cells. *Appl. Surf. Sci.* **2017**, *416*, 124–132.

(20) Liu, X.; Zhang, F.; Liu, Z.; Xiao, Y.; Wang, S.; Li, X. Dopant-Free and Low-Cost Molecular "Bee" Hole-Transporting Materials for Efficient and Stable Perovskite Solar Cells. *J. Mater. Chem. C* 2017, 5 (44), 11429–11435.

(21) Völker, S. F.; Vallés-Pelarda, M.; Pascual, J.; Collavini, S.; Ruipérez, F.; Zuccatti, E.; Hueso, L. E.; Tena-Zaera, R.; Mora-Seró, I.; Delgado, J. L. Fullerene-Based Materials as Hole-Transporting/ Electron-Blocking Layers: Applications in Perovskite Solar Cells. *Chem. - Eur. J.* **2018**, *24*, 8524–8529.

(22) Liu, X.; Rezaee, E.; Shan, H.; Xu, J.; Zhang, Y.; Feng, Y.; Dai, J.; Chen, Z.; Huang, W.; Xu, Z. Dopant-Free Hole Transport Materials Based on Alkyl-Substituted Indacenodithiophene for Planar Perovskite Solar Cells. J. Mater. Chem. C 2018, 6, 4706–4713.

(23) Liu, X.; Wang, Y.; Rezaee, E.; Chen, Q.; Feng, Y.; Sun, X.; Dong, L.; Hu, Q.; Li, C.; Xu, Z. Tetra-Propyl-Substituted Copper (II) Phthalocyanine as Dopant-Free Hole Transporting Material for Planar Perovskite Solar Cells. *Sol. RRL* **2018**, *2*, 1800050.

(24) Hu, Q.; Rezaee, E.; Dong, Q.; Shan, H.; Chen, Q.; Wang, L.; Liu, B.; Pan, J.; Xu, Z. P3HT/Phthalocyanine Nanocomposites as Efficient Hole-Transporting Materials for Perovskite Solar Cells. *Sol. RRL* **2019**, *3*, 1800264.

(25) Kim, G.-W.; Kang, G.; Kim, J.; Lee, G.-Y.; Kim, H. Il; Pyeon, L.; Lee, J.; Park, T. Dopant-Free Polymeric Hole Transport Materials for Highly Efficient and Stable Perovskite Solar Cells. *Energy Environ. Sci.* **2016**, *9* (7), 2326–2333.

(26) Kim, G. W.; Lee, J.; Kang, G.; Kim, T.; Park, T. Donor-Acceptor Type Dopant-Free, Polymeric Hole Transport Material for Planar Perovskite Solar Cells (19.8%). *Adv. Energy Mater.* **2018**, *8*, 1701935.

(27) Matsui, T.; Petrikyte, I.; Malinauskas, T.; Domanski, K.; Daskeviciene, M.; Steponaitis, M.; Gratia, P.; Tress, W.; Correa-Baena, J. P.; Abate, A.; Hagfeldt, A.; Grätzel, M.; Nazeeruddin, K. M.; Getautis, V.; Saliba, M. Additive-Free Transparent Triarylamine-Based Polymeric Hole-Transport Materials for Stable Perovskite Solar Cells. *ChemSusChem* **2016**, *9* (18), 2567–2571.

(28) Dubey, A.; Adhikari, N.; Venkatesan, S.; Gu, S.; Khatiwada, D.; Wang, Q.; Mohammad, L.; Kumar, M.; Qiao, Q. Solution Processed Pristine PDPP3T Polymer as Hole Transport Layer for Efficient Perovskite Solar Cells with Slower Degradation. *Sol. Energy Mater. Sol. Cells* **2016**, *145*, 193–199.

(29) Stolterfoht, M.; Wolff, C. M.; Amir, Y.; Paulke, A.; Perdigón-Toro, L.; Caprioglio, P.; Neher, D. Approaching the Fill Factor Shockley – Queisser Limit in Stable, Dopant-Free Triple Cation Perovskite. *Energy Environ. Sci.* **2017**, *10*, 1530–1539.

(30) Krishna, A.; Grimsdale, A. C. Hole Transporting Materials for Mesoscopic Perovskite Solar Cells – towards a Rational Design? J. Mater. Chem. A 2017, 5 (32), 16446–16466.

(31) Jiang, X.; Yu, Z.; Zhang, Y.; Lai, J.; Li, J.; Gurzadyan, G. G.; Yang, X.; Sun, L. High-Performance Regular Perovskite Solar Cells Employing Low-Cost Poly(Ethylenedioxythiophene) as a Hole-Transporting Material. *Sci. Rep.* **2017**, *7*, 42564.

(32) Perera, I. R.; Gupta, A.; Xiang, W.; Daeneke, T.; Bach, U.; Evans, R. A.; Ohlin, C. A.; Spiccia, L. Introducing Manganese Complexes as Redox Mediators for Dye-Sensitized Solar Cells. *Phys. Chem. Chem. Phys.* **2014**, *16* (24), 12021.

(33) Park, S. M.; Yook, K. S.; Lee, W. H.; Hong, Y.; Lee, J. Y.; Kang, I. N. Synthesis and Characterization of Thermally Crosslinkable Hole-Transporting Polymers for PLEDs. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51* (23), *5111–5117*.

(34) Neumann, K.; Schwarz, C.; Köhler, A.; Thelakkat, M. Influence of the Excited-State Charge-Transfer Character on the Exciton Dissociation in Donor–Acceptor Copolymers. *J. Phys. Chem. C* 2014, *118* (1), 27–36.

(35) Xu, X.; Zhu, Y.; Zhang, L.; Sun, J.; Huang, J.; Chen, J.; Cao, Y. Hydrophilic Poly(Triphenylamines) with Phosphonate Groups on the Side Chains: Synthesis and Photovoltaic Applications. *J. Mater. Chem.* **2012**, *22* (10), 4329.

(36) Zhang, X.; Cao, S.; Huang, L.; Chen, L.; Ouyang, X. Enhanced Three-Photon Absorption and Excited up-Conversion Fluorescence of Phenanthroimidazole Derivatives. *Dyes Pigm.* **2017**, *145*, 110–115. (37) Talipov, M. R.; Hossain, M. M.; Boddeda, A.; Thakur, K.; Rathore, R. A Search for Blues Brothers: X-Ray Crystallographic/ Spectroscopic Characterization of the Tetraarylbenzidine Cation

Spectroscopic Characterization of the Tetraarylbenzidine Cation Radical as a Product of Aging of Solid Magic Blue. Org. Biomol. Chem. 2016, 14 (10), 2961–2968. (38) Völker, S. F.; Dellermann, T.; Ceymann, H.; Holzapfel, M.;

(38) Volker, S. F.; Dellermann, T.; Ceymann, H.; Holzapfel, M.; Lambert, C. Synthesis, Electrochemical, and Optical Properties of Low Band Gap Homo- and Copolymers Based on Squaraine Dyes. J. Polym. Sci., Part A: Polym. Chem. **2014**, 52 (7), 890–911.

Κ

(39) Leijtens, T.; Ding, I. K.; Giovenzana, T.; Bloking, J. T.; McGehee, M. D.; Sellinger, A. Hole Transport Materials with Low Glass Transition Temperatures and High Solubility for Application in Solid-State Dye-Sensitized Solar Cells. *ACS Nano* **2012**, *6* (2), 1455– 1462.

(40) Deepa, M.; Salado, M.; Calio, L.; Kazim, S.; Shivaprasad, S. M.; Ahmad, S. Cesium Power: Low Cs $^+$ Levels Impart Stability to Perovskite Solar Cells. *Phys. Chem. Chem. Phys.* **2017**, *19* (5), 4069–4077.

(41) Xiang, X.; Shao, W.; Liang, L.; Chen, X.; Zhao, F.; Lu, Z.; Wang, W.; Li, J.; Li, W. Photovoltaic Poly(Rod-Coil) Polymers Based on Benzodithiophene-Centred A–D–A Type Conjugated Segments and Dicarboxylate-Linked Alkyl Non-Conjugated Segments. *RSC Adv.* **2016**, *6*, 23300–23309.