

Strategic Design, Synthesis, and Computational Characterization of Hole Transport Materials for Lead-Free Perovskite Solar Cells

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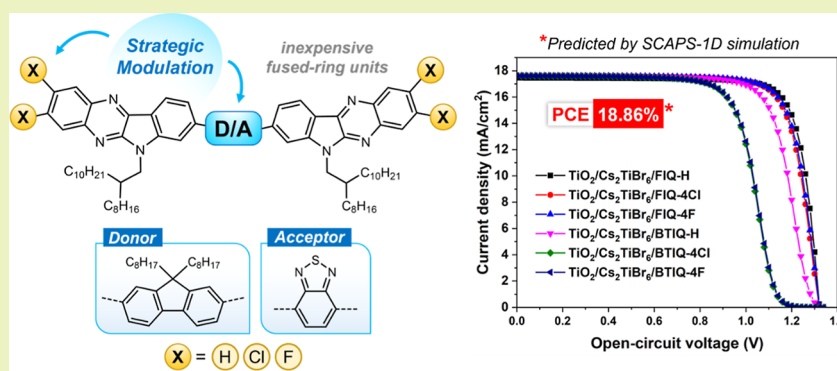
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ABSTRACT: Lead-free perovskites based on nontoxic titanium(IV) are promising candidates for photovoltaic applications due to their improved intrinsic/environmental stability compared to the lead analogues in metal halide perovskite solar cells (PSCs). However, their yet lower power conversion efficiencies (PCEs) predominantly owing to a lack of compatible charge transport layers limit their commercial viability. Here, we synthesized and characterized two series of hole-transporting materials (HTMs) based on fluorene and benzothiadiazole cores functionalized with halogen-substituted indoloquinoline arms. Employing experimental and first-principles density functional theory calculations, the structure–property relationships and electrochemical, optical, and charge transport characteristics of these HTMs were examined. The synthesized HTMs showed low-lying highest occupied molecular orbital (HOMO) energy levels at -5.73 to -6.04 eV having ideal band alignment with the cesium titanium(IV) bromide (Cs_2TiBr_6) perovskite material. The HTMs exhibited minimal absorption in the visible region ($\lambda_{\text{max}}^{\text{abs}} \leq 422$ nm) with negligible overlap with the photoactive perovskite absorber Cs_2TiBr_6 . Computational analysis further revealed the HTMs' ability to possess high charge separation and transfer potential, characterized by high charge hopping rates, robust mobility, and lower exciton binding energy compared to benchmark Spiro-OMeTAD. Photovoltaic device simulations using SCAPS-1D software projected promising performance for PSCs incorporating these HTMs, with open-circuit voltage (V_{OC}) ranging between 1.29 and 1.32 V and predicted PCE surpassing 18%. The study introduces a new class of HTM candidates with low-lying HOMOs and tailored electronic properties, presenting a compelling alternative to Spiro-OMeTAD for lead-free PSCs.

KEYWORDS: perovskite solar cells, hole transport materials, conjugated materials, indoloquinoline, density functional theory

1. INTRODUCTION

Organic–inorganic halide perovskite solar cells (PSCs) are promising candidates for next-generation photovoltaics due to their power conversion efficiencies (PCEs) exceeding 26% and low production costs, positioning them as viable alternatives to traditional silicon technologies.¹ Lead (Pb)-based perovskites, such as MAPbI_3 and FAPbI_3 , have demonstrated exceptional optoelectronic properties, including high absorption coefficients, long carrier diffusion lengths, and favorable bandgaps for solar energy conversion that contribute to their notable efficiencies in photovoltaic applications.² However, the environmental and stability concerns related to toxic Pb^{2+}

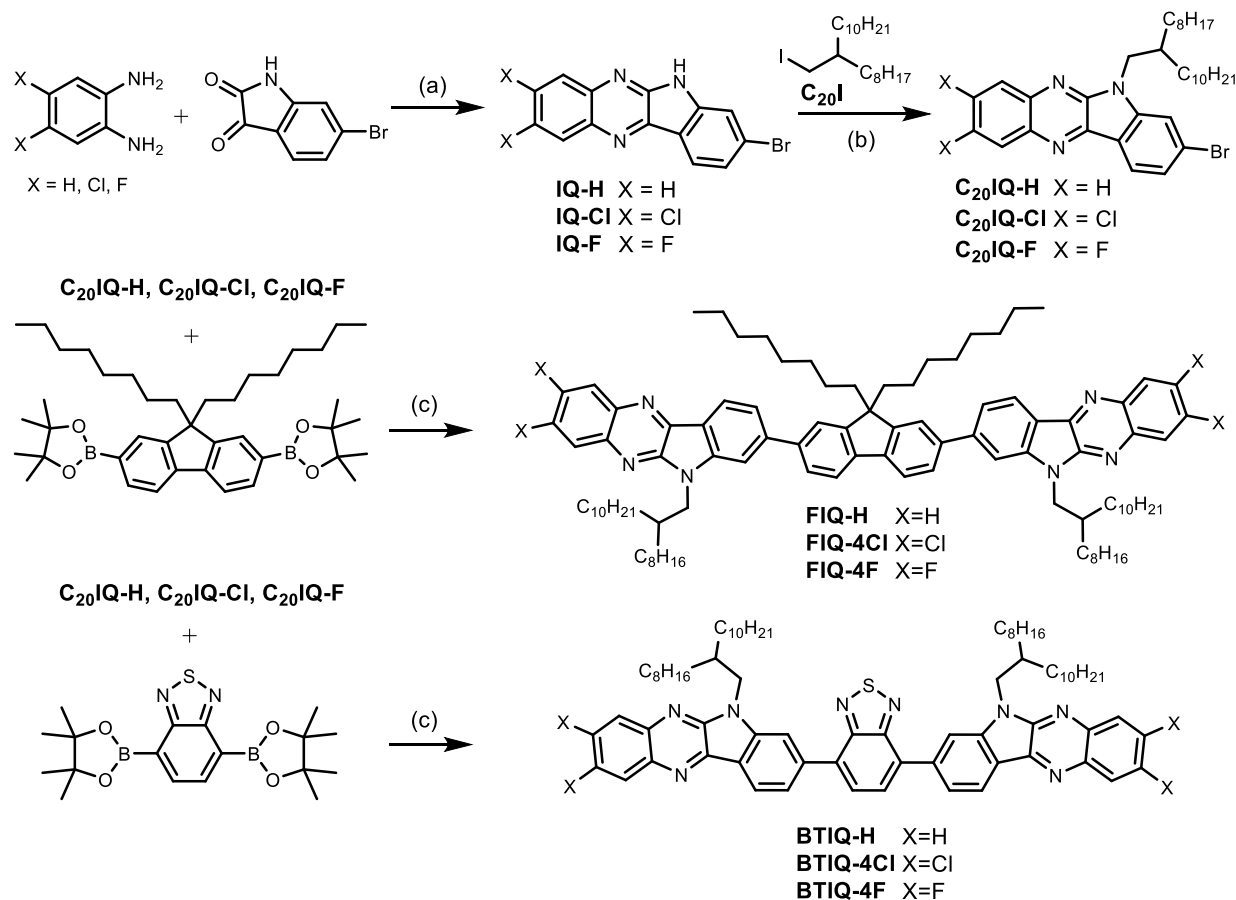
ions and volatile organic cations (e.g., MA^+ and FA^+) remain critical obstacles to their commercialization.^{3,4} These limitations highlight an urgent need for lead-free perovskite materials that provide comparable efficiency, stability, and environmental sustainability.

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Scheme 1. Synthesis Route of Fluorene-IQ (FIQ) and Benzothiadiazole-IQ (BTIQ) HTMs: (a) Acetic Acid, Dimethylformamide (DMF), Reflux Overnight; (b) 9-(Iodomethyl)nonadecane, K_2CO_3 , DMF, 120 °C, Overnight; and (c) $Pd(dba)_2$, K_2CO_3 , tris(*o*-Tolyl)phosphine, Aliquat 336, Toluene/Water, 80 °C, Overnight



While a range of lead-free perovskites has been explored, only a few materials have demonstrated the potential for both practical PCEs and stability. For instance, tin-based perovskites, such as $CsSnI_3$, offer an ideal bandgap (~ 1.3 eV) for single junction cells but face degradation issues due to rapid oxidation of Sn^{2+} , reducing material stability.^{5,6} Additionally, the potential toxicity of Sn-based compounds, as reported by Babayigit et al., further complicates their viability.⁷ Other lead-free alternatives, including bismuth (Bi^{3+}) and antimony (Sb^{3+})-based perovskites (e.g., $Cs_3Sb_2I_9$ and $Cs_3Bi_2I_9$), offer environmental stability and safety, but their wide bandgaps (> 2.0 eV) and low charge transport efficiencies limit their use in efficient solar cells.^{8–10} In this context, titanium (Ti)-based perovskites, especially cesium Ti(IV) bromide (Cs_2TiBr_6), offer a promising lead-free solution. Ti, in the stable +4 oxidation state, is earth-abundant, nontoxic, and resistant to environmental degradation, making it suitable for large-scale photovoltaic applications.^{11,12} Cs_2TiBr_6 , a vacancy-ordered double perovskite with a tunable bandgap, demonstrates stability under environmental stresses and exhibits an optical bandgap (~ 1.8 eV) appropriate for tandem and single-junction cells.^{13,14}

Early studies by Padture et al. have shown that Cs_2TiBr_6 -based devices can achieve PCEs of $\sim 3.3\%$ with enhanced environmental stability and favorable charge transport properties, such as balanced electron and hole diffusion lengths exceeding 100 nm, suggesting that the material could become a viable alternative to lead-based perovskites with further

optimization.¹⁵ Notably, the integration of commonly used charge transport layers, including poly(3-hexylthiophene) (P3HT) as a hole transport layer (HTL) and C_{60} as an interfacial layer between the Cs_2TiBr_6 film and the TiO_2 electron transport layer, has improved initial PCEs from 2.15% to higher values, demonstrating that interface engineering can significantly enhance device performance. However, despite these advances, Cs_2TiBr_6 -based PSCs continue to exhibit relatively low PCEs compared to lead-based perovskites, primarily due to limitations in charge transport layer compatibility and suboptimal band alignment.

To enhance Cs_2TiBr_6 PSC efficiency, effective hole-transporting materials (HTMs) are essential to facilitate charge extraction, minimize interfacial energy losses, and improve stability. While organic HTMs such as Spiro-OMeTAD, PTAA, and PEDOT have contributed to PSC advancements, they face challenges regarding cost, doping dependency, and stability.^{16,17} Recently, Wang et al. optimized a Cs_2TiBr_6 -based PSC utilizing poly(3-hexylthiophene) as an HTL, achieving a projected PCE of 16.86%.¹⁸ Yong et al. reported that indoloquinoline (IQ)-based HTMs enhance PSC performance by improving interfacial energy alignment and passivating defects. This enhancement leads to better charge extraction, resulting in a higher PCE of up to 20% and improved stability.¹⁹ Saltan et al. also demonstrated enhanced charge-transfer (CT) capabilities and optimization energy levels achieved through the incorporation of IQ in their molecular design.²⁰

In this study, we designed and synthesized novel HTMs featuring fluorene and benzothiadiazole (BT) cores with IQ side arms, as depicted in Scheme 1. Fluorene serves as a stable, conjugated backbone, providing a high hole mobility that is essential for efficient charge transport within the device architecture. Its rigid, planar structure promotes effective π - π stacking and enhances electronic coupling, crucial for maintaining optimal charge carrier dynamics.²¹ BT is a widely recognized electron acceptor that enhances energy level alignment, facilitating charge separation and significantly reducing recombination losses at the HTM/perovskite interface.²² The strong electron-withdrawing characteristics of BT contribute to lowering the highest occupied molecular orbital (HOMO) energy levels of the HTMs, aligning them favorably with the valence band maximum (VBM) of Cs_2TiBr_6 , thus promoting efficient hole extraction. IQ, included as a side arm, introduces tunable electronic properties and improves stability against environmental stressors, thereby enhancing both material robustness and device longevity. The versatility of IQ allows for further modifications, such as halogenation, enabling precise control over the electronic properties, intrinsic and interfacial charge carrier transport, chemical stability, and photoexcitation behavior. This tunability is critical for optimizing the performance of the HTMs in varying operational conditions.¹⁹ The strategic combination of these building blocks results in a tailored HTM architecture that is optimized for the specific requirements of the Cs_2TiBr_6 -based PSCs. Moreover, our cost-effective and scalable synthesis methods emphasize the utilization of inexpensive raw materials and facile, rapid reactions, enabling the large-scale production of these HTMs for commercial applications.²³

We employed a combination of experimental techniques and density functional theory (DFT) calculations to establish structure–property relationships of our HTMs, correlating computational predictions with the observed performance characteristics. SCAPS-1D simulations were used to model device-level performance, projecting high V_{OC} (1.29–1.32 V) and promising PCEs surpassing 18%. These findings suggest that our newly synthesized HTMs align well with Cs_2TiBr_6 , offering improved stability, efficient charge extraction, and enhanced performance. This study thus provides key insights into the design of sustainable, high-performance HTMs for lead-free PSCs, with the potential to advance the field toward more environmentally friendly and commercially viable photovoltaic technologies.

2. MATERIALS AND METHODS

2.1. Materials and Instruments. All chemicals utilized in the synthesis were procured from commercial sources and used without further purification. Detailed synthesis procedures can be referred to in Scheme 1, while detailed protocols are available in the Supporting Information. The ^1H and ^{13}C NMR spectra were obtained by using a Bruker AV3 400 MHz NMR spectrometer with chloroform- d as the solvent. UV–vis absorption spectra were recorded on a Cary 60 UV–vis spectrophotometer, while emission spectra were recorded using a Cary Eclipse Fluorescence Spectrophotometer in chloroform using a 2.5 $\mu\text{g/mL}$ sample. Cyclic voltammetry was performed using a PalmSens EmStat3+ potentiostat in a standard three-electrode setup, consisting of an Ag/AgCl reference electrode, a platinum wire counter electrode, and a glassy carbon working electrode.

2.2. Computational Details. **2.2.1. Quantum Calculations of HTMs.** First-principles DFT and time-dependent DFT (TD-DFT) in Gaussian 16 software were employed to investigate the structural, electronic, and photophysical properties of HTMs and the reference molecule Spiro-OMeTAD.^{24,25} The B3LYP hybrid functional in

conjunction with the 6-31G(d,p) basis set was employed to accurately describe the geometric and electronic properties.²⁶ Geometry optimization and electronic structure calculations were conducted iteratively until a convergence was achieved. TD-DFT calculations were carried out to simulate the photophysical profile and transition state phenomena. Furthermore, to assess the influence of the solvent environment on the HTMs, the solvation model IEFPCM was employed to calculate Gibbs solvation-free energy (ΔG_{solv}) and partition coefficients ($\text{Log } P_{\text{n-octanol/water}}$).²⁷ These calculations provided insights into the energetics of solvation and the stability of the HTMs in different environments during potential PSC fabrication.

Additionally, the electronic transition state phenomenon was investigated through hole–electron distribution/overlap analysis, charge density difference (CDD) surfaces, and amount of charge transferred (q_{ct}) during electronic excitations. This framework of analysis simulated through MultiWfn 3.8 provided insights into charge density variations between the ground state and excited state to quantify the CT excitations, which are critical for efficient exciton dissociation and intrinsic charge carrier mobility. Moreover, the independent gradient model (IGMH) isosurfaces and corresponding reduced-density gradient (RDG) scatter plots versus the Hessian eigenvalue multiplied by the electronic density were simulated to investigate the intermolecular interactions in the optimized dimer structures and their effect on charge carrier mobility parameters.^{28,29}

Marcus theory and the charge hopping model were simulated systematically to quantify critical parameters governing hole transport in the synthesized HTMs. In this context, the hole mobility (μ_{h}) was evaluated using the Einstein relation given in eq 1.³⁰

$$\mu_{\text{h}} = \frac{e r^2}{2K_{\text{B}}T} k_{\text{h}} \quad (1)$$

where k_{B} is the Boltzmann constant, T is the temperature, e is the electron charge, and K_{h} is the hole transport rate. K_{h} was calculated by the Marcus theory given in eq 2.

$$k_{\text{h}} = \frac{2\pi}{h} \frac{t_{\text{h}}^2}{\sqrt{4\pi\lambda_{\text{h}}K_{\text{B}}T}} \exp\left[-\frac{\lambda_{\text{h}}}{4K_{\text{B}}T}\right] \quad (2)$$

In this equation, λ_{h} is the hole reorganization energy and t_{h} is the hole transfer integral (t_{h}). Internal reorganization energy is a measure of the energy required for relaxation between the neutral and charge states, which has an inverse relation with the intrinsic charge transport. λ_{h} was calculated from the adiabatic potential surface relation based on the neutral and oxidized state energy of HTMs (given in eq 3).^{31,32}

$$\lambda_{\text{h}} = [E_{+}^0 - E_0] + [E_0^{+} - E_{+}] \quad (3)$$

whereas t_{h} was calculated from the direct coupling approach, which explains the charge hopping potential between neighboring monomers (given in eq 4).

$$t_{\text{h}} = \langle \phi_i^{0,\text{site1}} | F^0 | \phi_j^{0,\text{site2}} \rangle \quad (4)$$

Here, F^0 is the Fock operator of the dimer system, while $\phi_i^{0,\text{site1}}$ represents the HOMO and $\phi_j^{0,\text{site2}}$ represents the lowest unoccupied molecular orbital (LUMO) of adjacent molecules in the dimer system.

2.2.2. Device Model Numerical Simulations. Complementing DFT calculations and experimental characterizations, SCAPS 1D (version 3.3.07) was employed for numerical simulations of the photovoltaic device performance of proposed lead-free Cs_2TiBr_6 -based cells employing the synthesized HTMs.^{33,34} Device simulations were conducted using a planar, noninverted n–i–p device structure, focusing specifically on the effects of the HTMs on device performance, in the conventional FTO/ TiO_2 / Cs_2TiBr_6 /HTM/Au stack configuration. The device model was validated by the reported literature, and the performance of synthesized HTMs was studied in comparison to standard HTMs such as Spiro-OMeTAD, PEDOT:PSS, P3HT, and NiCo_2O_4 .

Table 1. Optical and Electronic Structure Parameters of Designed FIQ and BTIQ Series and Benchmark Spiro-OMeTAD HTM for Reference, Reported from Ref 42

molecule	E_H (eV) ^a	E_L (eV) ^a	E_g (eV) ^b	$\lambda_{\text{max}}^{\text{abs}}$ (nm) ^c	$\lambda_{\text{max}}^{\text{emi}}$ (nm) ^c	λ_{st} (nm) ^d	E_H (eV) ^e	E_g (eV) ^e	E_L (eV) ^e	E_X (eV) ^e	E_B (eV) ^e	q_{ct} (e) ^e
FIQ-H	−5.73	−2.89	2.83	392	490	98	−5.49	3.41	−2.08	3.04	0.37	0.79
FIQ-4Cl	−5.80	−3.07	2.72	413	506	93	−5.73	3.29	−2.44	2.92	0.37	0.71
FIQ-4F	−5.77	−3.00	2.77	400	498	98	−5.63	3.35	−2.27	2.99	0.36	0.72
BTIQ-H	−5.88	−3.26	2.62	415	510	95	−5.67	2.98	−2.68	2.57	0.41	0.59
BTIQ-4Cl	−6.04	−3.36	2.67	417	498	81	−5.97	3.02	−2.95	2.62	0.40	0.65
BTIQ-4F	−6.01	−3.35	2.64	422	500	78	−5.86	3.02	−2.83	2.62	0.40	0.61
Spiro-OMeTAD	−5.15	−2.20	2.95	384	420	36	−4.27	3.56	−0.71	3.05	0.51	0.59

^aEnergy level of HOMO and LUMO determined by the oxidation and reduction onsets by CV ($E_{\text{ox}}^{\text{onset}}$ and $E_{\text{red}}^{\text{onset}}$) by the relation $E_H = -(E_{\text{ox}}^{\text{onset}} - E_{\text{Fc}}^{\text{onset}} + 4.8)$ eV and $E_L = -(E_{\text{red}}^{\text{onset}} - E_{\text{Fc}}^{\text{onset}} + 4.8)$ eV. ^bOptical bandgap (E_g) determined by the relation $E_g = E_H - E_L$. ^cWavelengths of the absorption maxima ($\lambda_{\text{max}}^{\text{abs}}$) and emission maxima ($\lambda_{\text{max}}^{\text{emi}}$) of the HTM solutions in chloroform (2.5 $\mu\text{g/mL}$) at wavelengths of 410 nm. ^dStokes shift (λ_{st}) calculated from absorption and emission maxima difference. ^eTheoretically calculated energy level values, bandgap, S_0 – S_1 excitation energy (E_X), exciton binding energy (E_B), and total CT (q_{ct}) simulated with the TD-B3LYP/6-31G (d,p) method.

3. RESULTS AND DISCUSSION

3.1. Synthesis. IQ derivatives were synthesized by reacting 6-bromoindoline-2,3-dione with the respective 1,2-diaminobenzene in glacial acetic acid as the solvent, with DMF serving as the cosolvent, as previously reported.³⁵ High yields ranging from 80 to 84% were achieved. To mitigate solubility challenges attributed to the rigid fused-ring framework of IQs, N-alkylation was pursued using 9-(iodomethyl)nonadecane. 9-(Iodomethyl)nonadecane was first synthesized by gentle iodination of 2-octyl-1-dodecanol, using triphenylphosphine and 1H-imidazole in anhydrous dichloromethane, resulting in a yield of 83%. Subsequently, 9-(iodomethyl)nonadecane was used for N-alkylation of IQs in the presence of potassium carbonate base in anhydrous DMF, yielding alkylated IQs with consistent yields ranging from 74 to 81%.

The synthesis of FIQ and BT-IQ (BTIQ) series was achieved via palladium-catalyzed Suzuki–Miyaura cross-coupling reactions.³⁶ This involved the reaction of borylated cores (9,9-dioctyl-9H-fluorene-2,7-diboronic acid bis(pinacolate) ester or 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacolate ester)) with alkylated IQs in the presence of palladium(0) bis(dibenzylideneacetone) catalyst, tri(*o*-tolyl)phosphine ligand, and potassium carbonate base in a toluene/water solvent system. The desired products were obtained in satisfactory yields ranging from 70 to 80%. Structural elucidation of the major products was performed by using ¹H NMR and ¹³C NMR spectroscopy techniques (Figures S1–S15).

3.2. Electronic Structure and Electrochemical Properties. A suitable electronic structure of the HTMs is crucial for optimization of both the charge transport functionality and enhance the performance of PSCs.³⁷ The HOMO level (E_H) alignment of HTMs with the VBM of the perovskite material (e.g., −5.91 eV for Cs_2TiBr_6 perovskite) is critical for maximizing the V_{OC} .^{38,39} It enables efficient hole extraction and transport coupled with reduced interface recombination losses. Similarly, the LUMO level (E_L) must be significantly higher than the conduction band maximum (CBM) of the perovskite (e.g., −4.1 eV for Cs_2TiBr_6 perovskite) to block electron flow to the back-contact and mitigate hole–electron recombination.⁴⁰

Herein, to gain insights into the electronic structure and redox behavior of the HTMs and how the structural modifications influence oxidation onsets (E_{ox}) and reduction onsets (E_{red}), cyclic voltammetry (CV) and DFT calculations were carried out (Table 1). The CV measurements were performed in 5 mL of anhydrous dichloromethane containing

2 mM analyte and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte, with a scan rate of 50 mV/s. The electrochemical solutions were deoxygenated by purging with dry N₂ for 5 min. E_H and E_L were determined by correlating the oxidation and reduction onsets measured against ferrocene/ferrocenium ($E_{\text{ox}}^{\text{Fc}}/\text{Fc}^+$, $E_{\text{red}}^{\text{Fc}}/\text{Fc}^+$) to the normal hydrogen electrode, with the E_H of Fc/Fc^+ assumed to be 4.88 eV. The normalized CV profiles and the energy level diagram of the proposed PSC device structure of synthesized HTMs in comparison to benchmark Spiro-OMeTAD are shown in Figure 1a–c.

The CV data exhibited E_{ox} at 1.15 V and E_{red} at −1.67 V, respectively, for the FIQ-H molecule. FIQ-4Cl yielded a slightly decreased E_{red} at −1.49 V and an increased E_{ox} at 1.23 V, attributed to Cl atoms stabilizing the reduced form, whereas the introduction of F atoms exhibited E_{ox} to 1.20 V with comparatively higher E_{red} at −1.57 V in the FIQ-4F derivative. As a result, the E_H was exhibited as −5.73 eV for FIQ-H and with linear stabilization upon halogenation to −5.77 eV for FIQ-4F and −5.80 eV for FIQ-4Cl derivatives, respectively. It shows that the E_H values of FIQ series HTMs in the range −5.73 to −5.80 eV exhibit ideal energy level alignment with Cs_2TiBr_6 perovskite VBM (−5.91 eV), which is beneficial for efficient hole extraction and transport at interfaces, whereas the HTMs exhibited E_L well above the Cs_2TiBr_6 perovskite CBM (−4.1 eV) with values such as −2.89 eV for FIQ-H, −3.00 eV for FIQ-4Cl, and −3.07 eV FIQ-4F for effective electron blocking at the interfaces. The higher E_L is expected to reduce hole–electron recombination at the perovskite/HTM interface.⁴¹

In the BTIQ series of HTMs, the addition of Cl atoms in BTIQ-4Cl lowered the E_{red} to −1.21 V and raised the E_{ox} to 1.46 V as compared to the nonhalogenated BTIQ-H with E_{red} of −1.31 V and the E_{ox} value of 1.30 V, while the fluorinated BTIQ-4F yielded E_{red} at −1.21 V and E_{ox} at 1.43 V, with F atoms increasing the oxidation potential while keeping the reduction potential stable. BTIQ-H exhibited an E_H of −5.88 eV and an E_L of −3.26 eV, which are ideal in terms of band alignment for facilitating both efficient hole extraction and electron blocking. Both BTIQ-4Cl and BTIQ-4F exhibited lower E_H values with −6.04 and −6.01 eV, respectively, which hampers hole transport across the HTM due to the increased energy barrier at the interface, though they maintain effective electron blocking properties with E_L levels at −3.36 and −3.35 eV, respectively.

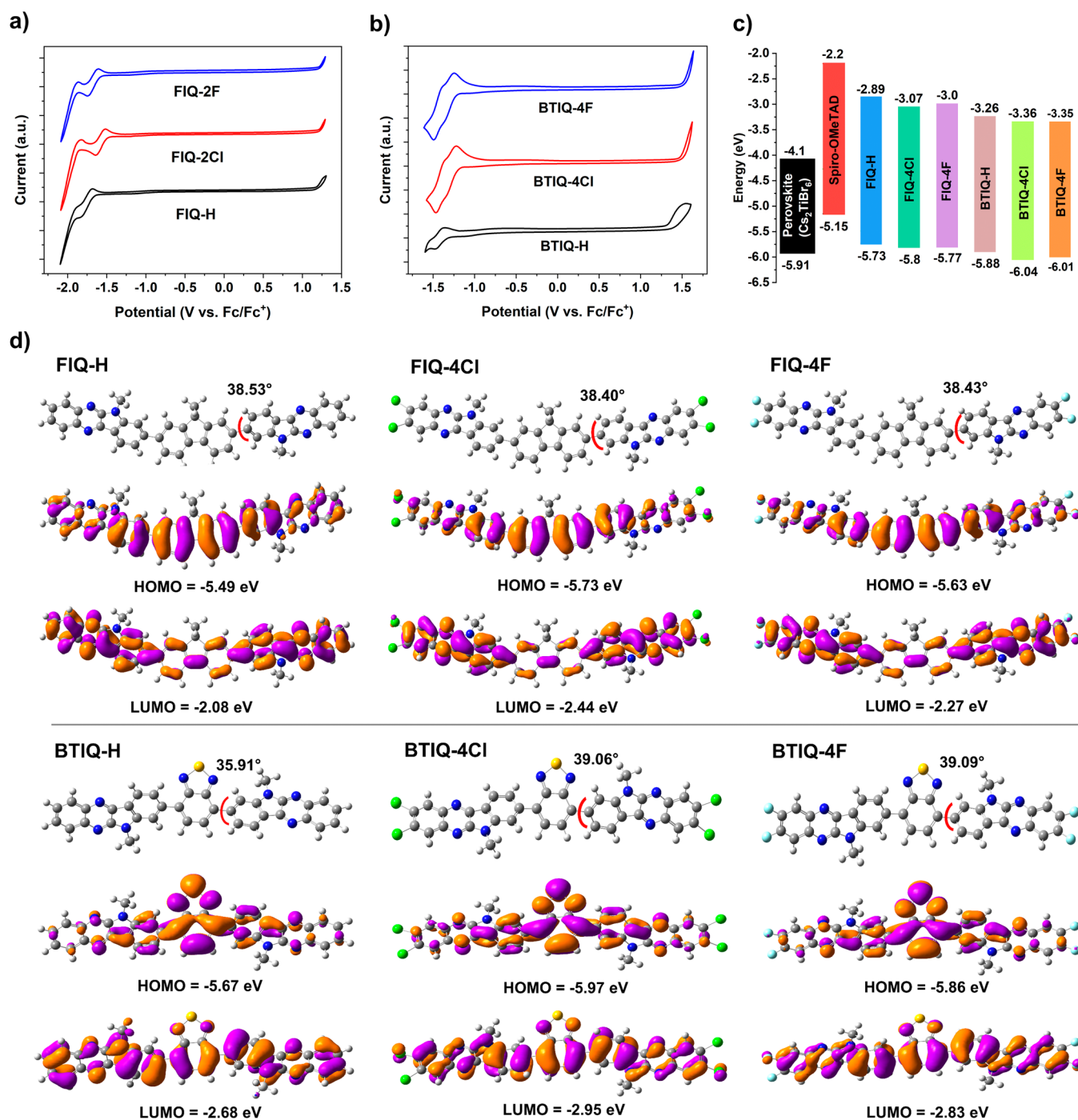


Figure 1. (a) Cyclic voltammograms of FIQ series; (b) cyclic voltammograms of BTIQ series; (c) energy level diagram of synthesized FIQ and BTIQ series estimated from CV measurements and benchmark Spiro-OMeTAD against the perovskite absorber layer for the proposed device structure; and (d) optimized geometries and corresponding frontier molecular orbital delocalization contours simulated B3LYP/6-31G(d,p) DFT method.

To further verify the electronic properties of the HTMs, the structural configuration, and charge density delocalization of the HOMO and LUMO orbitals, DFT calculations at the B3LYP/6-31G(d,p) method were performed. As illustrated in Figure 1d, the moderately higher dihedrals between the cores and IQ arms due to steric repulsion of neighboring hydrogen atoms demonstrated a quasi-coplanar geometry. The FIQ series consistently shows a dihedral angle around 38.5°, with minimal changes (38.40–38.43°) due to Cl and F substitutions.

In the BTIQ series, Cl and F substitutions result in angles of 39.04° and 39.06°, while the unsubstituted BTIQ-H has a slightly smaller angle of 35.9°, indicating slightly less twisting. Although torsional angles generally reduce HOMO and LUMO delocalization compared with planar structures, significant delocalization still occurs due to strong electronic coupling. In BTIQ series HTMs, LUMOs are concentrated on the BT core due to its higher electron-withdrawing ability compared to that of IQ arms. Conversely, in FIQ series HTMs,

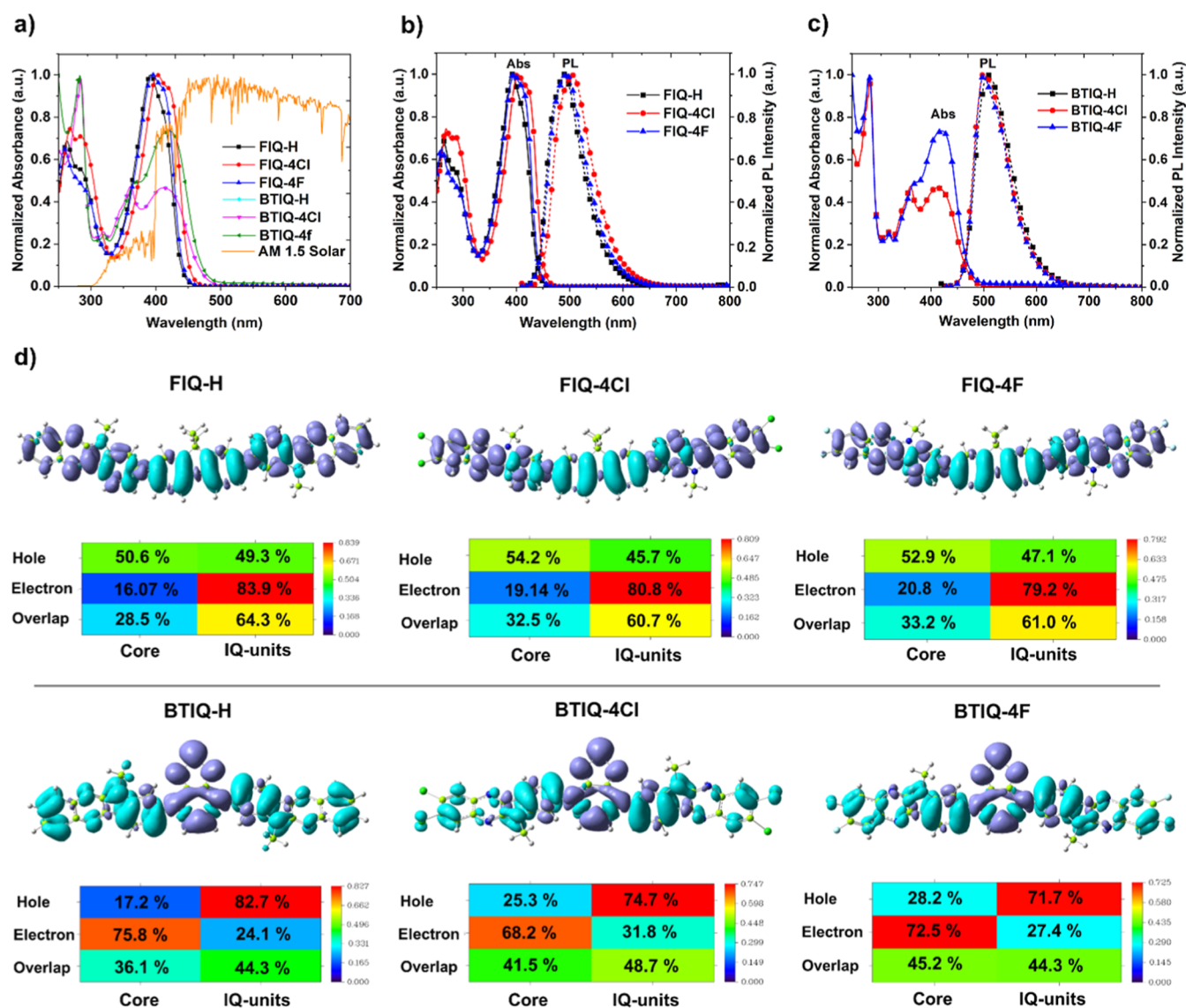


Figure 2. (a) Combined absorption spectra of HTMs compared with the solar spectrum (AM 1.5); (b) absorption and emission spectra of FIQ series in chloroform (2.5 $\mu\text{g/mL}$); (c) absorption and emission spectra of BTIQ series in chloroform (2.5 $\mu\text{g/mL}$); and (d) CDD contours showcasing hole delocalization with blue color and electron delocalization with cyan color, and the corresponding hole–electron delocalization and overlap heat maps of HTMs.

LUMOs are mainly delocalized over the IQ arms due to the lower electron-withdrawing ability of the fluorene core.

Moreover, the experimental E_{H} of FIQ-H/BTIQ-H measured from cyclic voltammograms (−5.73 eV/−5.88 eV) closely matched the predicted E_{H} (−5.49 eV/−5.67 eV) with the B3LYP/6-31G (d,p) method, with consistent trends in energy level stabilization upon halogenation of IQ arms and the electronic bandgaps in both FIQ and BTIQ series. This further reinforces the validation of the used DFT approach as well as its reliability in predicting structural parameters, energy level trends, and electrochemical properties of the synthesized HTMs.

3.3. Optical Properties. The optical properties of the synthesized HTMs were evaluated through UV–visible absorption and photoluminescence (PL) emission spectra, measured in chloroform solutions (2.5 $\mu\text{g/mL}$). The results are summarized in Table 1, and the corresponding spectra are presented in Figure 2a–c.

The BTIQ series exhibits red-shifted absorption maxima ($\lambda_{\text{max}}^{\text{abs}}$) compared to the FIQ series, with values ranging from 415 to 422 nm versus 392–413 nm, respectively. This shift is primarily attributed to enhanced intramolecular charge transfer (ICT) facilitated by the electron-accepting properties of the BT core, which lower the transition energy and stabilize the excited state. While both series benefit from a near-planar conformation and extended π -conjugation, the greater extent of ICT in the BTIQ compounds results in more significant red shifts relative to their fluorene-based FIQ counterparts.

Within the FIQ series, the unsubstituted compound FIQ-H exhibited a $\lambda_{\text{max}}^{\text{abs}}$ of 392 nm, slightly red-shifted from the $\lambda_{\text{max}}^{\text{abs}}$ of Spiro-OMeTAD at 384 nm. FIQ-4Cl displayed an absorption red-shift with $\lambda_{\text{max}}^{\text{abs}}$ at 413 nm, attributed to chlorine's strong electron-withdrawing effect. FIQ-4F absorption had a peak at 400 nm, indicating a lesser impact of fluorine substitution. In the BTIQ series, BTIQ-H yielded $\lambda_{\text{max}}^{\text{abs}}$ at 415 nm, reflecting the intrinsic red-shift of the series. Among its derivatives, BTIQ-4F exhibited the most pronounced red-shift with a peak at 422

Table 2. Calculated Adiabatic Ionization Potential (IP_a), Electron Affinity (EA_a), Chemical Hardness (η), Solvation-Free Energy (ΔG_{solv}) in Dichloromethane Solvent, and Distribution Coefficient ($\text{Log } P_{n\text{-octanol/water}}$) with the B3LYP/6-31G (d,p) DFT Method

molecule	IP_a (eV)	EA_a (eV)	η (eV)	ΔG_{solv} (kcal/mol)	$\text{Log } P_{n\text{-hexane/water}}$
FIQ-H	6.35	1.28	2.53	−8.70	11.69
FIQ-4Cl	6.86	1.49	2.68	−8.88	14.33
FIQ-4F	6.48	1.48	2.50	−8.32	12.15
BTIQ-H	6.56	1.73	2.42	−8.44	8.55
BTIQ-4Cl	6.82	2.07	2.37	−8.66	11.19
BTIQ-4F	6.76	1.91	2.40	−8.11	9.01
Spiro-OMeTAD ^a	4.47	1.09	1.69	−15.05	16.22

^aDFT calculations of Spiro-OMeTAD “B3LYP/6-31G(d,p)” are given for reference.

nm, highlighting fluorine’s role in enhancing ICT, while BTIQ-4Cl, with an absorption maximum of 417 nm, showed a reduced influence of chlorine on ICT compared to its effect in the FIQ series.

Overall, the results suggest that variation of the core unit and peripheral halogenation strategy HTMs effectively modulates the electronic structure, resulting in small but notable red-shifts in $\lambda_{\text{max}}^{\text{abs}}$ (2–21 nm range). Additionally, both FIQ and BTIQ series HTMs show minimal spectral overlap with the visible region of the A.M. 1.5 solar spectrum (450–750 nm), where the perovskite absorber operates, is shown in the combined spectra in Figure 2a. This characteristic allows the perovskite layer to remain the primary photon absorber in PSC devices, an important feature for enhancing overall device efficiency.

The PL spectra of FIQ and BTIQ series HTMs showed red-shifted emission maxima ($\lambda_{\text{max}}^{\text{emi}}$) relative to the benchmark Spiro-OMeTAD. The FIQ series displayed emission peaks between 490 and 506 nm, with chlorinated and fluorinated derivatives showing progressive red shifts due to enhanced ICT effects.⁴³ In the BTIQ series, the $\lambda_{\text{max}}^{\text{emi}}$ ranged from 510 to 522 nm, with halogenation also inducing slight blue shifts (10–12 nm) relative to the unsubstituted BTIQ-H, as the electron-withdrawing halogens on IQ balance the donor–acceptor ICT in this core.

Stokes shifts for these HTMs, calculated as the difference between the $\lambda_{\text{max}}^{\text{abs}}$ and $\lambda_{\text{max}}^{\text{emi}}$ spanned from 78 to 98 nm, significantly larger than 36 nm in the case of Spiro-OMeTAD. This indicates higher structural flexibility in both series, which can facilitate efficient pore filling and improved film morphology in PSCs.⁴⁴ Enhanced ICT and structural adaptability in the HTMs are thus expected to contribute to more uniform and stable perovskite films, benefiting the overall PSC performance.

To further investigate the photophysical profiles of the synthesized HTMs, TD-DFT calculations were performed to simulate the ICT mechanisms upon photoexcitation. The CDD contours with corresponding hole–electron distribution heat maps were simulated with the TD-B3LYP/6-31G (d,p) method, whereas the optical properties for excited-state $S_0 \rightarrow S_1$ electronic transitions including excitation energy (E_x), exciton binding energy (E_b), and q_{ct} during electronic transitions are summarized in Table 1, and parameters for the first five excited states including absorption wavelength (λ), oscillatory strength (f), transition dipole moment (μ_{tran}), and molecular configuration interaction are given in Supporting Information Tables S1–S5.

The experimental $\lambda_{\text{max}}^{\text{abs}}$ for the FIQ and BTIQ series (404–425 nm) closely matched the TD-DFT simulated values (407–432 nm) with the TD-B3LYP/6-31G (d,p) method with

good consistency in trends and absolute values. This further underscore the reliability of our simulations in precise estimation of the photoinduced electronic density transition phenomena. The CDD maps presented in Figure 2d show different charge density patterns in HTMs. In the FIQ series, holes are almost equally delocalized over the electron-donating fluorene core and IQ units, while electrons concentrate on the IQ arms (79.2–83.9%), reducing the hole–electron overlap (28.5–64.3%) for low E_b to improve charge separation and decrease the charge recombination losses. In BTIQ series, the trend is reversed with electron density focusing on the electron-deficient BT core (68.2–75.8%) and holes spreading out on the IQ arms (71.7–82.2%), resulting in low spatial hole–electron overlap (36.1–48.7%) at the core and IQ arms.

Overall, the HTMs showed uniform CDD distributions, aiding efficient charge delocalization and prominent ICT processes attributed to lower spatial hole–electron overlap and π – π^* electronic transitions and stronger electronic coupling between cores and IQ arms. The TD-DFT calculation results for the first five excited-state transitions are given in the Supporting Information, Tables S1–S5. Moreover, the q_{ct} representing the total charge transferred during electronic transitions showed varying values among HTMs due to different molecular architectures, with the FIQ series typically higher (0.71–0.79 e) compared to the BTIQ series (0.59–0.61 e). This is due to enhanced electronic coupling in FIQ series facilitating efficient CT, whereas slightly lower conjugation and weaker coupling potentially reduces CT efficiency in BTIQ series. However, their values are comparable to or slightly better than Spiro-OMeTAD, suggesting promise for their use as HTLs.

In addition to the efficient ICT characteristics, a low E_b of HTMs is crucial for efficient charge carrier dissociation. The lower E_b values, observed in studied HTMs (0.36–0.41 eV), compared to those in Spiro-OMeTAD (0.51 eV), suggested easier exciton dissociation and charge extraction. This aligns with the lower overlap between holes and electrons in CDD contours and hole–electron heat maps. Overall, FIQ and BTIQ series demonstrated lower absorption in the visible region, larger Stokes shifts, uniform CDD distributions, higher q_{ct} and lower E_b values, indicating efficient intrinsic charge carrier transfer and robust exciton dissociation. These traits make the synthesized HTMs promising candidates for application in lead-free PSCs, offering low parasitic losses, improved pore-filling capabilities, and reduced recombination losses, thereby supporting an enhanced device performance and stability.

3.3.1. Processability and Chemical Stability. HTMs must possess excellent solubility, chemical stability, and hydro-

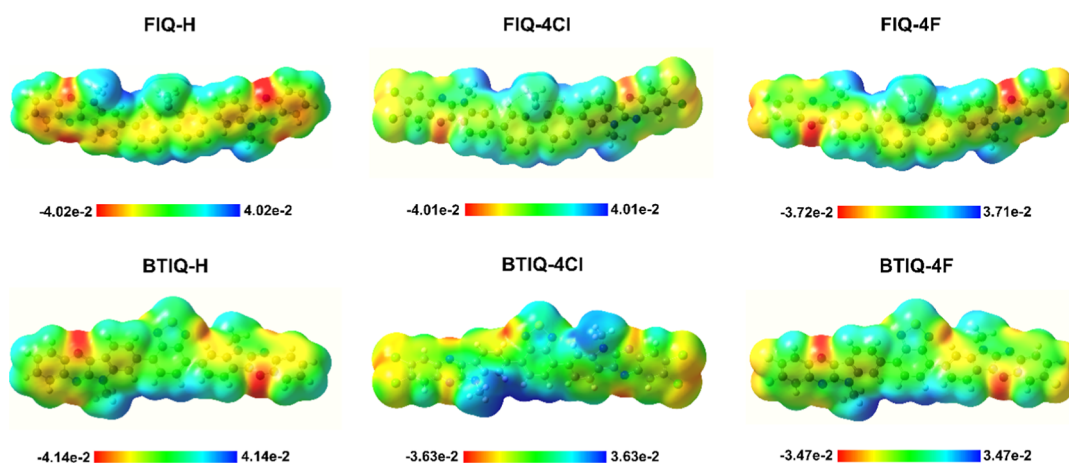


Figure 3. MESP surface contours of designed FIQ and BTIQ series HTMs.

phobicity for ease of processability of thin films and higher operational stability.³⁷ Herein, parameters such as Gibbs solvation-free energy (ΔG_{solv}), chemical hardness (η), and partition coefficient ($\text{Log } P_{n\text{-hexane/water}}$) were simulated through the B3LYP/6-31G (d,p) DFT method. ΔG_{solv} indicates solubility and extent of film formation capability. The results are summarized in Table 2. Employing chlorobenzene as a solvent medium, FIQ-H exhibited a slightly better ΔG_{solv} of -8.70 kcal/mol compared to BTIQ-H, with ΔG_{solv} of -8.44 kcal/mol, due to its planar core that favorably interacts with the solvent. FIQ-4Cl demonstrated superior solubility with a ΔG_{solv} of -8.88 kcal/mol compared to -8.32 kcal/mol shown by FIQ-4F substitutions, likely owing to the increased polarizability of Cl atoms, which improves interaction with slightly polar solvents such as chlorobenzene. The trend is similar in the case of the BTIQ series, with BTIQ-4Cl and BTIQ-4F showing ΔG_{solv} values of -8.66 and -8.11 kcal/mol, respectively. Spiro-OMeTAD demonstrates excellent solubility with an ΔG_{solv} of -15.05 kcal/mol in chlorobenzene owing to its highly symmetrical and electron-rich structure. However, in practical applications, studied HTMs with large alkyl chains on IQ arms may have an advantage in outperforming Spiro-OMeTAD.

The chemical stability of HTMs was assessed by the chemical hardness (η) which is calculated by the difference between adiabatic ionization potential (IP_a) and adiabatic electron affinity (EA_a).⁴⁵ FIQ-H, FIQ-4Cl, and FIQ-4F demonstrated chemical hardnesses of 2.53, 2.68, and 2.50 eV, respectively. The higher hardness of FIQ-4Cl is attributed to the larger size and polarizability of Cl atoms, which differently contribute to overall molecular stability by pulling electron density toward themselves. BTIQ-H, BTIQ-4Cl, and BTIQ-4F exhibit η values of 2.42, 2.37, and 2.40 eV, respectively. The inherent electron deficiency of the BT core governs the impact of substitutions and seems to limit the influence of Cl and F substitutions. Overall, all HTMs demonstrate higher η values than Spiro-OMeTAD (1.69 eV), indicating an increased resistance to alterations in electron distribution and enhanced stability against degradation processes. Furthermore, the hydrophobicity of HTMs was estimated from the $\text{Log } P_{n\text{-octanol/water}}$ based on the ratio of solvation energy of HTMs in octanol ($E_{n\text{-octanol}}$) to water (E_{water}).⁴⁶ Higher and positive values of $\text{Log } P_{n\text{-octanol/water}}$ indicate a higher hydrophobicity and hence their potential to improve solar cell durability and resistance to moisture-

induced degradation. The fluorene core and IQ units provide a hydrophobic backbone due to their sp^2 -hybridized carbon atoms and fused ring structure. FIQ-H shows a $\text{Log } P_{n\text{-octanol/water}}$ value of 11.69. The introduction of Cl and F atoms into FIQ-based HTMs enhances hydrophobicity, with $\text{Log } P_{n\text{-octanol/water}}$ values of 14.33 and 12.15 for FIQ-4Cl and FIQ-4F, respectively. The electron-withdrawing nature of halogens increases the overall lipophilicity of the molecule, driving it to preferentially partition into the nonpolar octanol phase. BTIQ series, despite containing additional nitrogen and sulfur atoms, are also hydrophobic due to their conjugated and rigid structure. Halogenation further increases hydrophobicity, with $\text{Log } P_{n\text{-octanol/water}}$ of 11.19 for BTIQ-4Cl and 9.01 for BTIQ-4F, compared to 8.55 for BTIQ-H. Overall, the designed HTMs having positive and higher $\text{Log } P_{n\text{-octanol/water}}$ are expected to have higher hydrophobic characteristics and hence better environmental stability for PSCs.

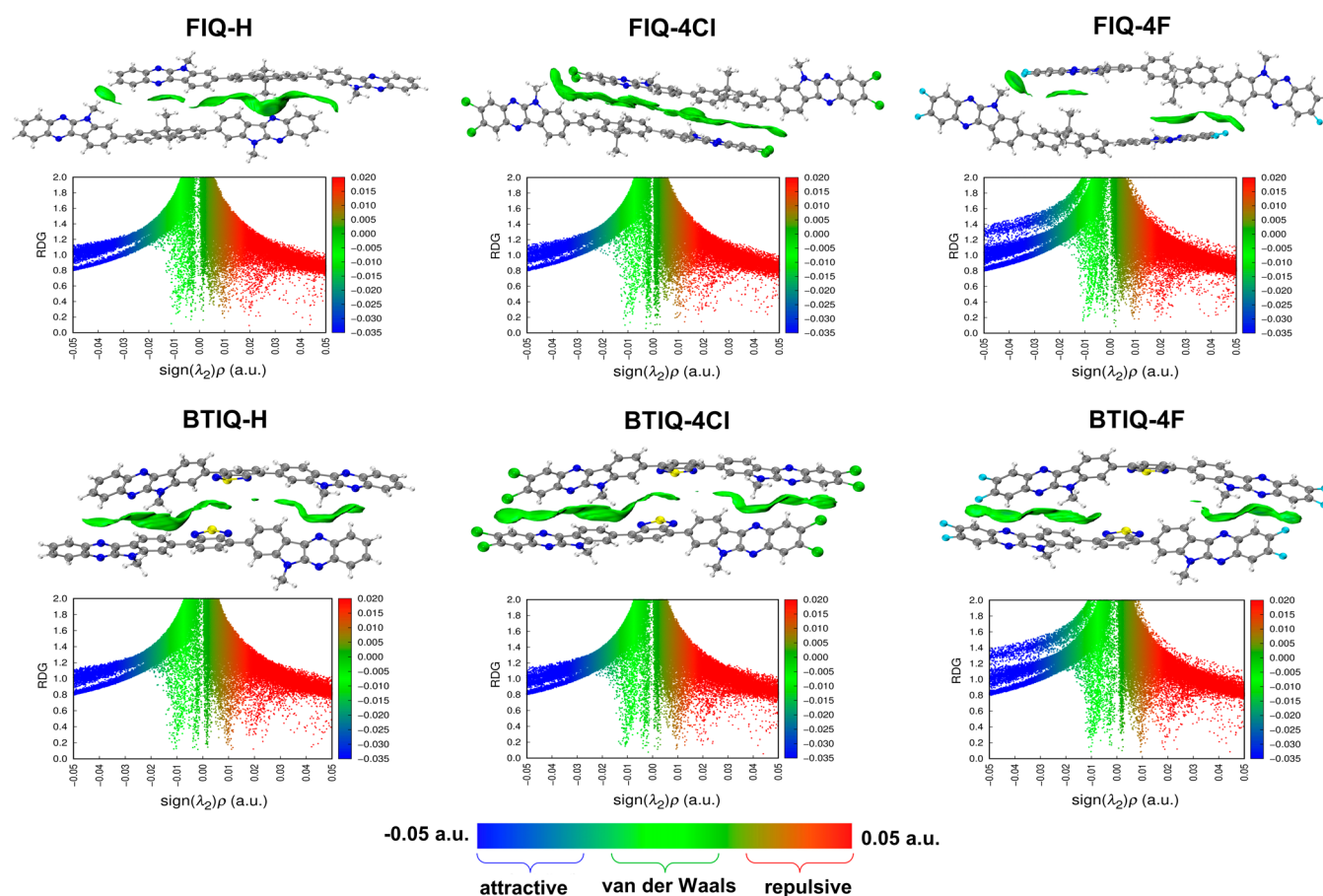
Additionally, the molecular electrostatic potential (MESP) maps of the HTMs reveal the distribution of charge across the molecular framework, emphasizing areas of negative potential typically surrounding electronegative atoms such as nitrogen, oxygen, and halogens as shown in Figure 3. Regions with higher electron density exhibit greater resistance to nucleophilic attacks and oxidative degradation, ensuring stability crucial for prolonged performance in PSCs. These regions show minimal charge density fluctuation upon structural modification, indicating a stable electronic environment and higher oxidation resistance, consistent with the chemical hardness findings discussed earlier. Overall, the HTMs demonstrate promising characteristics across these essential criteria, making them strong candidates for improving the performance and stability of PSCs.

3.3.2. Hole Mobility. High hole mobility (μ_h) is essential for efficient charge transport in PSCs to improve the device performance parameters such as short-circuit current density (J_{sc}) and fill factor (FF).⁴⁷ It enables rapid mobility of holes in the HTLs, aiding efficient charge extraction and transport to the electrode. Factors like hole reorganization energy (λ_h) and hole transfer integral (t_h) influence hole mobility.⁴⁸ The hole transport parameters were simulated based on Marcus theory and the charge hopping model.⁴⁹

To facilitate an accurate comparison of the designed HTMs with Spiro-OMeTAD, we calculated all charge transport parameters using the B3LYP/6-31G(d,p) method. While theoretical results for the HTMs can be directly compared to

Table 3. Calculated Hole Reorganization Energy (λ_h), Centroid-to-Centroid Distances (r), Hole Transfer Integral (t_h), Charge Hopping Rate (K_h), and Hole Mobility (μ_h) of the Designed HTMs by the B3LYP/6-31G (d,p) Method^a

molecule	λ_h (eV)	r (Å)	t_h (eV)	K_h (S ⁻¹)	μ_h (cm ² V ⁻¹ s ⁻¹)
FIQ-H	0.173	4.61	0.0287	6.17×10^{12}	2.55×10^{-1}
FIQ-4Cl	0.208	4.69	0.0210	2.16×10^{12}	9.25×10^{-2}
FIQ-4F	0.213	4.02	0.0219	2.19×10^{12}	6.89×10^{-2}
BTIQ-H	0.161	4.08	0.0287	7.19×10^{12}	2.33×10^{-1}
BTIQ-4Cl	0.201	4.25	0.0322	5.49×10^{12}	1.93×10^{-1}
BTIQ-4F	0.191	4.19	0.0219	2.87×10^{12}	9.81×10^{-2}
Spiro-OMeTAD ^a	0.131	11.19	0.0022	6.45×10^{10}	5.22×10^{-3}

^aDFT calculations of Spiro-OMeTAD “B3LYP/6-31G(d,p)” are given for reference.**Figure 4.** IGMH isosurfaces and the corresponding RDG scatter plots showcasing the intermolecular interactions in optimized dimer structures of FIQ and BTIQ series HTMs, simulated by MultiWfn 3.8.

experimental data for Spiro-OMeTAD, variability among data sources may introduce bias. Therefore, we adopted a two-step approach. First, we validated the methodology by computing the μ_h of Spiro-OMeTAD, which yielded a theoretical value of 5.22×10^{-3} cm² V⁻¹ s⁻¹, closely aligning with the experimental value of 1.30×10^{-3} cm² V⁻¹ s⁻¹. The calculated results also aligned well with μ_h calculations reported in recent theoretical studies.^{50,51} Subsequently, we employed this method to evaluate the μ_h of all HTMs relative to Spiro-OMeTAD. The results are summarized comprehensively in Table 3, and optimized dimer structures are shown in Figure S17.

λ_h is directly related to the electronic structure of the molecular system, and a lower λ_h suggests higher hole transport ability. The planarity and extended conjugation in FIQ-H facilitate efficient hole delocalization, leading to a low λ_h value of 0.173 eV, indicative of minimal energy barriers for hole

transfer through resonance stabilization. However, introducing Cl and F atoms alters the π -conjugation pattern along the IQ arms, resulting in increased λ_h values of 0.208 eV for FIQ-4Cl and 0.213 eV for FIQ-4F. The combination of the BT core with IQ units facilitates efficient hole transport, resulting in a lower λ_h of 0.161 eV compared to FIQ-H. This can be attributed to the presence of vacant π^* orbitals associated with the BT core, which stabilize positive charge, thereby reducing the energy barrier for hole transport. Similar to FIQ series, the introduction of Cl and F atoms on IQ units leads to higher λ_h values of 0.201 and 0.191 eV for BTIQ-Cl and BTIQ-F, respectively.

Besides the lower λ_h value, higher t_h is another crucial parameter influencing the overall μ_h of HTMs and is related to the centroid-to-centroid distances (r) reflecting intermolecular π - π stacking and van der Waals interactions via orbital

Table 4. Summary of Device Figures of Merit Based on Previously Reported Lead-Free (Cs_2TiBr_6) Perovskite as an Absorber Layer with Standard P3HT, PEDOT:PSS, Spiro-OMeTAD, NiCo_2O_4 , and Our Newly Designed Molecules as Hole Transport Layers through Numerical Simulations in SCAPS-1D

device structure	study	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)	refs
FTO/C60/ Cs_2TiBr_6 /P3HT/Au	Exp.	1.02	5.69	56.4	3.28	15
AZO/ TiO_2 / Cs_2TiBr_6 /PEDOT:PSS/Au	Sim.	1.38	18.20	71	17.83	58
TiO_2 / $\text{Cs}_2\text{AgBi}_{0.75}\text{Sb}_{0.25}\text{Br}_6$ /Spiro-OMeTAD/Au	Sim.	1.07	12.9	82.25	11.40	59
FTO/ TiO_2 / Cs_2TiBr_6 / NiCo_2O_4 /Au	Sim.	1.34	17.67	82.51	19.30	38
FTO/ TiO_2 / Cs_2TiBr_6 /FIQ-H/Au	Sim.	1.32	17.62	81.03	18.86	this work
FTO/ TiO_2 / Cs_2TiBr_6 /FIQ-4Cl/Au	Sim.	1.32	17.62	78.20	18.21	this work
FTO/ TiO_2 / Cs_2TiBr_6 /FIQ-4F/Au	Sim.	1.32	17.62	78.72	18.33	this work
FTO/ TiO_2 / Cs_2TiBr_6 /BTIQ-H/Au	Sim.	1.32	17.62	73.94	17.21	this work
FTO/ TiO_2 / Cs_2TiBr_6 /BTIQ-4Cl/Au	Sim.	1.29	17.61	63.73	14.47	this work
FTO/ TiO_2 / Cs_2TiBr_6 /BTIQ-4F/Au	Sim.	1.30	17.61	64.56	14.79	this work
Shockley–Queisser limit for E_g 1.8 eV	Sim.	1.49	19.65	91.4	26.86	60

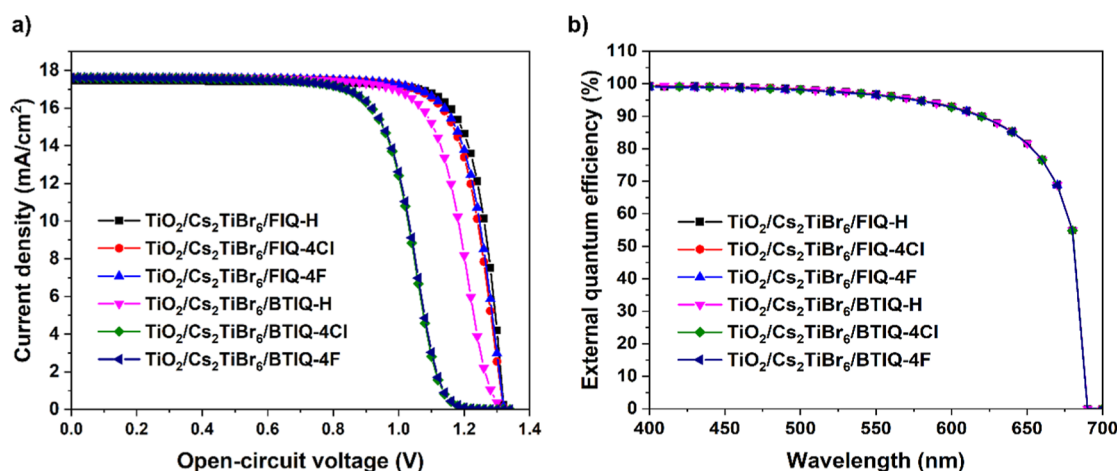


Figure 5. (a) Short-circuit current density versus the open-circuit voltage and (b) external quantum efficiency from conventional FTO/ TiO_2 / Cs_2TiBr_6 /HTM/Au stack configuration simulated via SCAPS 1D device simulations for the FIQ and BTIQ series.

overlaps for high hole hopping rate (K_h).^{29,52,53} To investigate the intermolecular interactions in the dimer structures of synthesized HTMs, we simulated the IGMH isosurface contours and the corresponding RDG scatter plots through MultiWfn 3.8 software. As shown in Figure 4, the green patches between neighboring HTM molecules in the IGMH isosurfaces of dimers and low-density gradient area in the corresponding RDG plots showed the nonbonding orbital overlap. This implies that the intermolecular π - π stacking in the HTM dimers is due to van der Waals interactions, which are further optimized upon halogenation of peripheral IQ arms.

The r of the FIQ-H system was estimated to be 4.61 Å, and t_h was in the order of 0.0287 eV, yielding a K_h of $6.17 \times 10^{12} \text{ S}^{-1}$. This is indicative of strong coupling and faster charge hopping due to efficient π - π stacking as a result of near-planar structures. Introducing Cl atoms increased r to 4.69 Å but decreased t_h to 0.0210 eV, resulting in a lower K_h of $2.16 \times 10^{12} \text{ S}^{-1}$, likely due to weakened stacking from steric hindrance. In the FIQ-4F system, r decreased to 4.02 Å, possibly due to the smaller size of F atoms, with t_h at 0.0219 eV and K_h at $2.19 \times 10^{12} \text{ S}^{-1}$. F atoms may enhance stacking via additional C-H $\cdots$ F and F $\cdots\pi$ interactions as indicated by the pronounced green patches in the isosurfaces contours, potentially boosting charge hopping. BTIQ-H possessed a moderate r of 4.08 Å and a t_h of 0.0287 eV, similar to its FIQ-based counterpart, resulting in a high K_h of $7.19 \times 10^{12} \text{ S}^{-1}$.

Addition of Cl atoms on IQ units slightly increased both r , 4.25 Å, and t_h , 0.0322 eV, leading to a moderate decrease in K_h , $5.49 \times 10^{12} \text{ S}^{-1}$. The higher t_h value suggests stronger π - π stacking, potentially due to favorable C-H $\cdots$ Cl interactions. The BTIQ-4F system had a similar r , 4.19 Å, to the unsubstituted counterpart BTIQ-H, with a lower t_h , 0.0219 eV, and reduced K_h , $2.87 \times 10^{12} \text{ S}^{-1}$, likely due to enhanced F-induced intermolecular interactions enhancing π - π stacking and charge hopping. Comparatively, the Spiro-OMeTAD HTM shows a much larger r , 11.19 Å, indicating weaker π - π stacking interactions, likely due to the spirocyclic twisted core. This results in a notably lower t_h of 0.0022 eV, suggesting weaker intermolecular electronic coupling, which leads to a low K_h of $6.45 \times 10^{10} \text{ S}^{-1}$.

Overall, the Spiro-OMeTAD yielded a low μ_h at $5.22 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, consistent with its large r and low t_h , reflecting weaker π - π stacking interactions and inefficient charge hopping. Investigated HTMs, especially FIQ-H and BTIQ-H, show the highest μ_h among the designed HTMs, with values of 2.55×10^{-1} and $2.33 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Both molecules share similar electronic characteristics, including short r and t_h , promoting efficient charge hopping. Chlorinated analogues, FIQ-4Cl and BTIQ-4Cl, have decreased μ_h of 9.25×10^{-2} and $1.93 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ compared to their unsubstituted variant, with FIQ-4Cl showing higher μ_h than BTIQ-4Cl. Both FIQ-4F and BTIQ-4F have μ_h of 6.89×10^{-2} and $9.81 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, indicating

improvements over Spiro-OMeTAD despite lower values than their unsubstituted counterparts. Overall, the designed HTMs exhibited robust hole mobility and are considered promising candidates for efficient PSCs.

3.3.3. Solar Cell Performance. We implemented the HTM materials in the solar cells and evaluated their performance using a numerical simulation tool. The PCE of solar cells is influenced by three key parameters: V_{OC} , J_{SC} , and FF. The intrinsic properties of the HTMs, such as energy level alignment, suitable electrochemical and optical properties, higher μ_h , significantly impact the cell's performance; however, the quality of the interface between the HTM and the photoactive perovskite layer is equally critical.⁵⁴ We used the SCAPS 1D numerical device simulations, in line with the previous reports,^{55–57} and estimated the optimized device performance of the proposed lead-free Cs_2TiBr_6 -based PSCs using FTO/ TiO_2/Cs_2TiBr_6 /HTM/Au stack configuration. The device simulation parameters are given comprehensively in Supporting Information Table S6.

The figures of merit given in Table 4 and the corresponding current–voltage curves and external quantum efficiency plots depicted in Figure 5a,b reflect that the device performance of the FIQ-based series was influenced by structural changes. The figures of merit presented in Table 4 reflect that the device performance cells based on FIQ series and BTIQ series HTMs were significantly influenced by structural modifications. From the results, the FIQ-H-based device exhibited a V_{OC} of 1.32 V, with a high FF of 81.03% and a resulting PCE of 18.86%, reflecting its excellent energy level alignment, electrochemical property compatibility, and efficient charge transport properties. The performance of the FIQ-4Cl-based device was slightly lower with a comparable V_{OC} of 1.32 V, an FF of 78.20%, and a PCE of 18.21%. Interestingly, the FIQ-4F-based device maintained a V_{OC} of 1.32 V and demonstrated an improved FF (78.72%), leading to a slightly higher PCE of 18.33%. These results suggest that the fluorinated and chlorinated variants retain good compatibility with the Cs_2TiBr_6 absorber layer, with moderate gains in efficiency attributed to their intrinsic properties expected in real devices.

In comparison, the BTIQ-based devices showed slightly reduced performance metrics. The nonhalogenated BTIQ-H based device achieved a V_{OC} of 1.32 V and an FF of 73.94%, resulting in a PCE of 17.21%, whereas the BTIQ-4Cl and BTIQ-4F HTMs exhibited small decreases in V_{OC} to 1.29 and 1.30 V, respectively, and lower FF of 63.73% and 64.56%, with corresponding PCEs of 14.47% and 14.79%. These results highlight that halogenation in the BTIQ series does not enhance device performance to the same extent as in the FIQ series, possibly due to differences in molecular configuration and nonideal band alignment because of highly down-shifted HOMOs compared to VBM of perovskite, which can increase charge recombination losses and reduce interfacial charge transport properties as also indicated by the respective lower current density.

When compared with the simulated performance parameters of the standard HTMs in a consistent device configuration, the synthesized HTMs performed favorably. For instance, devices with FIQ-H and FIQ-4F achieved PCEs of 18.86% and 18.33%, respectively, which are competitive with traditional HTMs like PEDOT (17.83%) and $NiCo_2O_4$ (19.30%). Moreover, the newly synthesized HTMs also demonstrated higher V_{OC} values relative to the initial Cs_2TiBr_6 -based planar heterojunction devices using P3HT (1.02 V) and showed

efficient charge transport similar to that of the benchmark Spiro-OMeTAD, which exhibited a high FF of 82.25%. Overall, these simulations using SCAPS-1D offer a first-principles-based evaluation, showcasing the potential of strategically designed newly synthesized FIQ and BTIQ series of HTMs in optimizing device performance for lead-free Cs_2TiBr_6 or its modified analogues with comparable band structures. It is worth noting that the Shockley–Queisser limit for a bandgap of 1.8 eV sets an idealized upper limit of 26.86% PCE, with a theoretical V_{OC} of 1.49 V and an FF of 91.4%, indicating that there is still room for optimization in future material designs for sustainable energy solutions.

4. CONCLUSIONS

In conclusion, this study presents a comprehensive exploration of new HTMs based on fluorene and BT cores integrated with IQ side arms. Our strategic design of these materials not only optimizes their electronic properties for enhanced stability against environmental stressors but also promotes scalability and cost-effectiveness in synthesis, paving the way for commercial applications. The findings reveal that the HTMs achieved optimal HOMO energy levels (−5.73 to −6.04 eV) that align favorably with the VBM of the Cs_2TiBr_6 perovskite, facilitating efficient hole extraction and transport. The HTMs also demonstrated significant improvements in photophysical properties, including red-shifted λ_{max}^{abs} (398–422 nm) and λ_{emi}^{abs} (490–510 nm), attributed to enhanced ICT, negligible overlap with the photoactive perovskite absorber Cs_2TiBr_6 , and larger Stokes shifts, indicative of greater structural flexibility that can enhance pore-filling and overall morphology in PSCs.

Moreover, the HTMs displayed uniform charge distribution and robust charge carrier dynamics, with q_{ct} values competitive with or superior to those of the benchmark Spiro-OMeTAD. The designed HTMs showcased increased hydrophobicity due to their structural characteristics, contributing to their potential for superior environmental stability in PSC applications. Hole mobility measurements revealed that our synthesized HTMs, particularly FIQ-H and BTIQ-H (0.255 and 0.233 $cm^2 V^{-1} s^{-1}$, respectively), outperform Spiro-OMeTAD, demonstrating promising values that indicate their potential for efficient charge transport. SCAPS-1D simulations further corroborated these findings, predicting a high V_{OC} of 1.29–1.32 V, FF on the order of 63.73–81.03%, and PCE exceeding 18%.

Further studies could expand the molecular architecture of designed HTMs by introducing alternative peripheral substitutions and additional heterocyclic rings within the IQ framework to optimize charge transport properties and stability. Exploring new donor–acceptor pairings may also enhance molecular planarity and stacking, widening the applicability across different lead-free perovskite compositions. Additionally, investigating the integration of these HTMs with diverse device components, including electron transport layers and back contacts, will be essential for assessing their operational durability and commercial potential. These directions will support the ongoing development of efficient and environmentally stable PSCs for sustainable photovoltaic applications.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.4c07415>.

Detailed experimental procedures for the synthesis of the new HTMs, including characterization data and simulation results supporting the findings in the main manuscript (PDF)

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Notes

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