Covalent Organic Framework-Incorporated MAPbl₃ for Inverted Perovskite Solar Cells with Enhanced Efficiency and Stability

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mobility were improved in the MAPbI₃ films when the COF was incorporated, particularly with the TPBTz-COF, compared to the original MAPbI₃ film. The photovoltaic performance and stability of the PVSCs containing the COF were enhanced compared to the PVSCs based on pristine MAPbI₃. The structure of the inverted PVSCs included indium tin oxide/NiO_x/COF (TPTP-COF, TPBT-COF, or TPBTz-COF):MAPbI₃/PC₆₁BM/bathocuproine/Ag. TPBTz-COF exhibited the highest power conversion efficiency (PCE) among the COF additives, achieving a PCE of 20.04%, an open-circuit voltage of 1.04 V, a short-circuit current density of 24.26 mA cm⁻¹, and a fill factor of 79.40%. The TPBTz-COF-based PVSC maintained 80% of its original power conversion efficiency after being stored for 400 h under ambient conditions (30 °C; 60% relative humidity).

KEYWORDS: triazine, covalent organic framework, MAPbI₃, photovoltaic, perovskite solar cell

1. INTRODUCTION

Organic-inorganic halide perovskite solar cells (PVSCs) are gaining significant interest due to their quick and continuous improvement in photoelectronic conversion efficiencies (PCEs) over a short time frame.^{1,2} The high PCEs of PVSCs can be attributed to their exceptional absorption intensity, high charge mobility, weakly bonded excitons that easily separate into free charges, and long carrier diffusion lengths in the perovskite film.^{3,4} However, the high PCE and long-term stability of PVSCs were constrained by crystal defects in the perovskite film.^{5,6} Perovskite crystals may exhibit crystal defects such as undercoordinated halide ions, undercoordinated Pb²⁺ ions, lead clusters, Pb-I antisite defects (PbI₃), and vacancies of I or MA.7-11 In order to enhance the efficiency and durability of PVSCs, different additives have been added to perovskite films to reduce crystal defects and enhance the performance and stability of the PVSCs.^{12–17}

Covalent organic frameworks (COFs) are porous crystalline materials made up of organic building blocks connected by robust covalent bonds.^{18–20} Highly porous and conjugated COFs with large specific surface areas, high crystallinity, and

efficient charge generation/separation and transportation are being widely studied for their potential applications in photocatalysis, energy storage devices, and photovoltaic solar cells.^{21–23} The optical properties of COFs, such as visible light absorption intensity, energy band gap, and band edge, can be adjusted by altering the chemical structure of building blocks.²⁴ COF with exceptional light-harvesting capability enhances photoinduced current densities and power conversion efficiency when integrated into the perovskite layer of PVSCs.²⁵ The ordered and conjugated framework, along with strong π - π interactions in the two-dimensional (2D) COF layers, enhance charge separation and transportation within the COFs. This is crucial for electron and hole transfer between the COF and perovskite interfacial layer.²⁶ Charge

Received:July 30, 2024Revised:September 8, 2024Accepted:September 10, 2024Published:September 19, 2024







Figure 1. Chemical structures of the TPTP-COF, TPBT-COF, and TPBTz-COF.

separation in a COF with donor–acceptor (DA) groups can be facilitated by photoinduced charges through intermolecular charge transfer, effectively reducing charge recombination and enhancing charge separation efficiency.²⁷ Furthermore, the frameworks of the COFs can serve as a template for the crystal growth of perovskite, enhancing the crystallinity, morphology, and stability of perovskite materials. Mohamed and colleagues

found that incorporating the COF at the $NiO_x/perovskite$ junction can enhance the formation and development of perovskite crystals, potentially decreasing charge recombination at the interface caused by defects.²⁸ He et al. found that the presence of 2D COF nanosheets in perovskite film slows down the movement of molecules between layers and causes perovskite crystals to increase in size along (110) planes.²⁹ 2D COF nanosheets located at the grain boundaries decrease defect density and enhance carrier transport within the perovskite film. The exceptional characteristics of the perovskite film contribute to the high PCE and outstanding stability of PVSC. So far, only a small number of COFs have been utilized as additives in the perovskite layer for PVSCs. The impact of the chemical structure, conjugation length, and particle size of the COF on the photovoltaic (PV) performance of PVSC has not been fully explored.

We created three triazine-based COF materials (TPTP-COF, TPBT-COF, and TPBTz-COF) in this research to enhance the quality of perovskite films and the PV performance of PVSCs by using them as additives in the methylammonium lead iodide (MAPbI₃) layer. Figure 1 displays the chemical structures of the three COFs. The COFs were synthesized through the Schiff base reaction of triazine core with triazine (TPTP-COF), benzotrithiophene (TPBT-COF), and benzobisthiazole (TPBTz-COF). The electron-accepting triazine-based n-type unit, with a planar structure and three phenyl groups, promotes the creation of highly crystalline structures.²² The creation of an imine-based bridge between the triazine units extends the π -electron conjugation and improves the electrical conductivity of the resulting TPTP-COF. The benzotrithiophene in the TPBT-COF acts as an electron-donor, while triazine serves as the electron-acceptor unit.²⁶ The incorporation of the TPBT-COF with DA structure into the MAPbI₃ layer was anticipated to improve the efficiency of charge transport and separation in the PVSC. The TPBTz-COF utilizes sulfur and nitrogencontaining benzobisthiazole as a p-type conjugated bridge between triazine units to enhance conjugation intensity and improve defect passivation in the perovskite layer. The study will explore how the particle size of the COF affects the morphology and photophysical properties of the COF/ MAPbI₃ layer, in addition to considering the chemical structure and conjugation length of the COFs. An investigation was conducted on the combined impacts of TPTP-COF, TPBT-COF, and TPBTz-COF on the morphology and photoelectronic characteristics of the MAPbI₃ layer, as well as the PV performance of inverted PVSCs. This study utilized SEM microscopy, X-ray diffractometer, ultraviolet-visible (UV-vis) absorption spectroscopy, photoluminescence spectroscopy (PL), time-resolved photoluminescence spectroscopy (TRPL), and charge mobility measurements. The PVSCs containing TPBTz-COF demonstrated higher power conversion efficiency and stability in comparison to PVSCs incorporating TPTP-COF and TPBT-COF.

2. EXPERIMENTAL DETAILS

2.1. Materials. The 2,4,6-tris(4-formylphenyl)-1,3,5-triazine (TPT-3CHO), benzo[1,2-b:3,4-b':5,6-b"]trithiophene-2,5,8-trialde-hyde (BTT-3CHO), Benzo[1,2-d:4,5-d]bisthiazole-2,6-diamine (BTz-2NH₂), *n*-BuOH, *o*-dichlorobenzene (*o*-DCB), 1-methyl-2-pyrrolidone (NMP), AcOH, mesitylene, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and other chemicals were purchased from Eextnsion, Aldrich, Chemsoon, Alfa, Acros, and TCI Chemical and used as received. The 2,4,6-tris(4-aminophenyl)triazine (TPT-3NH₂) and TPTP-COF were synthesized following methods described in a previous publication.²² The synthesis of TPBT-COF is illustrated in Scheme S1.²⁶ The TPBTz-COF was created by condensing a Schiff base according to Scheme S2.

The electro-transporting material 6,6-phenyl- C_{60} -butyric acid methyl ester (PC₆₁BM) was purchased from Unionward and used exactly as received. Acros supplied the Bathocuproine (BCP).

Methylammonium iodide (MAI), lead iodide (PbI_2), and various reagents and chemicals were bought from Acros, Aldrich, and TCI Chemical, and utilized without further processing. *N,N*-Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and chlorobenzene (CB) were distilled using drying agents and purged with nitrogen before being used.

2.2. Characterization of the COF- and COF/MAPbl₃ Blend-Based Perovskite Films. The HORIBA FT-720 FTIR spectrometer was used to record Fourier transform infrared (FTIR) spectra. The Varian Unity Inova spectrometer was used to record ¹³C NMR spectra at a frequency of 150 MHz. The thermogravimetric analysis (TGA) using PerkinElmer Pyrisl was used to determine the thermal decomposition temperatures (T_d) , which is the temperature at which the weight loss reached 10%, for both the monomers and COFs. The TGA analysis was performed in a nitrogen (N_2) atmosphere with a heating rate of 10 °C min⁻¹. The surface areas and pore characteristics of the COFs were measured using a surface area and porosity analyzer (ASAP 2010, Micromeritics). The UV-vis absorption spectra of the COF in an ethanol solution were measured using a Hitachi U3010 UV-vis spectrometer. The specific surface areas of the COFs were estimated using the Brunauer-Emmett-Teller (BET) method, while the Barret-Joyner-Halenda (BJH) method was used to estimate the pore size distributions. Materials Studio software was used to conduct theoretical simulations of the crystal structures of the COFs. The chemical compositions of the COFs and COF/MAPbI3 blends in perovskite films were analyzed using X-ray photoelectron spectroscopy (XPS) with a ULVAC-PHI PHI500 VersaProbe instrument. The structures of the COFs and COF/MAPbI₃ blends in perovskite films were examined using field emission scanning electron microscopy (FESEM, JSM 7401F; JEOL, Japan) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-1400). The morphologies of the COF/MAPbI₃ layers were imaged using atomic force microscopy (AFM, Seiko SII SPA400), performed in the tapping mode. The dynamic light scattering (DLS) method (Litesizer DLS 100) was used to measure the particle size distribution of the COFs (1 mg) in 10 mL of DMF/DMSO (4/1, v/v) solvent and MAI/PbI₂ solution. The DLS measurement samples were prepared by subjecting the COF solution to ultrasonic treatment at room temperature for a duration of 2 h.

The X-ray diffractometry (XRD) technique was used to analyze the crystalline structures of the perovskite films based on COFs and COF/MAPbI₃ blends. The analysis was performed using a Rigaku RINT 2000 instrument from Tokyo, Japan, with Ni-filtered Cu K α radiation. The UV–vis spectrometer was used to record the absorption spectra of the COFs and COF/MAPbI₃ blends in perovskite films that were coated on bare glass. The Hitachi F-4500 fluorescence spectrophotometer was used to record the photoluminescence (PL) spectra. The COF/MAPbI₃ blends based perovskite films coated on bare glass were analyzed using a Horiba Fluoromax-4 spectrometer and a Delta Time TCSPC-MCS kit with 405 nm pulsed LED light to measure the time-resolved PL (TRPL) spectra.

2.3. Fabrication and Characterization of PVSCs. The PVSCs in this study had the following structure: FTO-deposited glass/NiO_x/ COF:MAPbI₃/PC₆₁BM/BCP/Ag (100 nm), with the MAPbI₃ layer incorporated with a COF (TPTP-COF, TPBT-COF, or TPBTz-COF). Solaronix supplied the FTO-deposited glass (with a resistance of 7 Ω square⁻¹) that was acquired. After thorough washing, the FTO substrates of PVSCs featuring patterned electrodes were subsequently purified via O2 plasma treatment. In order to prepare the NiO, precursor solution, 100 mg of nickel(II) acetate tetrahydrate was dissolved in isopropanol and ethanolamine. The solution was stirred at 70 °C for multiple hours, and subsequently passed through a polytetrafluoroethylene-based filter. By spin-coating the NiO_x precursor solution, the FTO layer was coated with the NiO, -based HTL. Following a 10 min drying period at 80 $^\circ\text{C},$ the sample underwent a 60 min thermal treatment at 450 °C. The thickness of the NiO_x layer is approximately 10-20 nm.³⁰

 PbI_2 (1290.83 mg) and MAI powder (445.12 mg) were combined while stirring in a solution of DMF and DMSO (4/1, v/v). Additionally, 0.5 mg of COF was dissolved in 1 mL of a mixture solution of DMF and DMSO (4/1, v/v). Subsequently, 2 mL of the precursor solution based on MAI/PbI₂ was supplemented with 0, 3, 6, and 10 μ L of the COF dispersion solution (1 mg in 2 mL of DMF/ DMSO mixed solvent) while being continuously stirred at 85 °C for 2 h. The HTL-coated FTO substrate was coated with the resulting solution, which was deposited onto it through spin-coating the perovskite precursor solution containing COF at 2000 rpm for 1 min. 0.4 μ L CB as an antisolvent was then dropped in the middle of the films at 40 s before the end of spin coating. For 10 min, the substrate was dried on a hot plate at 100 °C. The perovskite films incorporated with 3, 6, and 10 μ L of TPTP-COF solution are designated as TPTP-3, TPTP-6, and TPTP-10, correspondingly; those incorporated with TPBT-COF in the same volume are designated as TPBT-3, TPBT-6, and TPBT-10; and those incorporated with TPBTz-COF in the same volume are designated TPBTz-3, TPBTz-6, and TPBTz-10, respectively. Next, a solution of PC₆₁BM in CB (20 mg mL⁻¹) was deposited on top of the MAPbI₃ layer by spin-coating at 2000 rpm for 30 s. Postheat treatment for $PC_{61}BM$ was carried out at 100 °C for 10 min. A solution (0.3 mL) of BCP in isopropanol (0.5 mg mL⁻¹) was subsequently deposited on top of the PC₆₁BM layer. BCP was first employed as the interface buffer layer between the PC₆₁BM and Ag layers to improve the performance of PVSCs. The Ag-based cathode was thermally deposited onto the $PC_{61}BM$ layer within a high-vacuum chamber. The PVSC exhibited an active area of 0.08 cm². The measurement of cathode deposition rate was conducted utilizing a Sycon STM-100/MF quartz thickness monitor. In order to ascertain the thicknesses of the thin films, a surface texture analysis system (3030ST, Dektak) was utilized. In order to determine the photovoltaic (PV) characteristics of the PVSCs, a programmable electrometer (Keithley 2400) was utilized in conjunction with current and voltage sources to simulate solar light (100 mW cm⁻²) from an AM1.5 solar simulator (NewPort Oriel 96000).

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization of TPBT-COF and TPBTz-COF. Schemes S1 and S2 illustrate the synthetic routes that we followed in order to obtain the TPBT-COF and TPBTz-COF, respectively. The TPBT-COF and TPBTz-COF were produced by means of one-pot Schiff base (imine) condensations between triazine cores (TPT-3NH₂ or TPT-3CHO) and BTT-3CHO or BTz-2NH₂, respectively, over a period of 3 days at 120 °C using n-BuOH/o-DCB or NMP/ mesitylene with AcOH as the catalyst. The TPBT-COF and TPBTz-COF samples that were produced synthetically exhibited solubility in widely used organic solvents, such as n-BuOH, o-DCB, NMP, DMF, and DMSO. The chemical structures of TPBT-COF and TPBTz-COF were determined by employing solid state ¹³C NMR spectroscopy and FTIR, respectively. The FTIR spectra of TPT-3NH₂, BTT-3CHO, TPBT-COF, BTz-2NH₂, and BTz-COF are illustrated in Figure S1. The signals of the aromatic amino $(ArNH_2)$ groups of TPT-3NH₂ were observed at 3200-3460 cm⁻¹ in Figure S1a. At 1615 and 817 cm⁻¹, respectively, the bending and outof-plane bending peaks of the N-H bonds in TPT-3NH₂ were observed. At 1500 cm⁻¹, the stretching peak of the aromatic ring C=C was observed. The stretching signal of the C=O in aldehyde groups was detected at 1664 cm-1 for BTT-3CHO. An extensive absorption band spanning from 2782 to 2896 cm⁻¹ was ascribed to the stretching of C-H bonds in BTT-3CHO aldehyde groups. The TPBT-COF spectrum exhibited the absence of signals corresponding to the aromatic amino and aldehyde groups subsequent to Schiff base (imine) condensation of TPT-3NH₂ and BTT-3CHO. At 1571 cm⁻¹, an absorption peak of imino (C=N) groups was observed. Two absorption peaks were observed in Figure S1b

corresponding to the aldehyde units of PT-3CHO at 2825 and 2725 cm⁻¹. At 1707 cm⁻¹, the signal for the C=O groups in TPT-3CHO was observed. At 3269 and 3383 cm⁻¹, two signals of N-H stretching in ArNH₂ groups were observed for BTz-2NH₂. The TPBTz-COF spectrum exhibited the absence of signals corresponding to the aromatic amino and aldehyde groups subsequent to Schiff base condensation of TPT-3CHO and BTz-2NH₂. At 1629 cm⁻¹, a peak representing C=N groups appeared.

The solid state ¹³C NMR spectra of TPBT-COF and TPBTz-COF are illustrated in Figure S2. A signal at 168 ppm was observed in the spectrum of TPBT-COF, corresponding to the carbon nuclei within the triazine core (carbon atom a). At 152 ppm, the signal of the carbon atom f of the imino groups became apparent. At 148 ppm, the signals of carbon atom e were detected, whereas at 142 ppm, those of carbon atoms i and j were observed. Furthermore, the carbon atoms b, c, d, and g emitted signals within the range of 120-140 ppm. At 115 ppm, the signals of carbon atom h became apparent. Furthermore, the TPBTz-COF spectrum exhibited a downfield signal corresponding to the carbon atom an of the triazine core, measuring approximately 170 ppm. The carbon atom signals f and g appeared at 162 and 167 ppm, respectively, in TPBTz-COF. At 140 ppm, the signal of the carbon atom e became apparent. At 123-143 ppm, the signals of the carbon atoms b, c, d, e, and i were detected. At 113 ppm, the signal of the carbon atom j became apparent.

The surface compositions and chemical structures of TPBT-COF and TPBTz-COF were analyzed by XPS. Four distinct peaks in the XPS survey spectrum depicted in Figure S3a indicated the presence of the elements C, N, S, and O. The C 1s, N 1s, and S 2p peaks were generated by the TPBT-COF skeleton's carbon, nitrogen, and sulfur atoms, respectively. The four peaks observed in the C 1s XPS spectrum at 284.2, 284.3, and 286.5 eV are ascribed to the C=C bonds present in the phenyl groups, the S-C=C bonds in the thiophene groups, and the C=N-C bonds in the imino groups, respectively, as shown in Figure S3b. The N 1s binding energy signal was divided into three distinct peaks at 397.6, 398.2, and 400.2 eV [Figure S3c]. These peaks correspond to the N atoms situated in the imino bonds, the C=N bonds in the triazine rings, and the dangling -NH₂ bonds, respectively.³¹ The S 2p spectrum exhibits two distinct peaks, denoted as S $2p_{3/2}$ and S $2p_{1/2}$, respectively, at 163.5 and 164.7 eV [Figure S3d]. At 531.4 eV, a weak peak for the O 1s binding energy was observed. Based on these observations, it can be inferred that the COF fragment contained only a limited number of unreacted aldehyde groups of TPT-3CHO at its extremities.

Figure S4 illustrates the presence of additional peaks at C 1s, N 1s, S 2p, and O 1s in the XPS spectrum of TPBTz-COF. Three peaks at 284.1, 284.3, and 286.5 eV in the deconvoluted XPS spectrum for the C 1s orbitals corresponded to the C=C bonds in the phenyl groups, the S-C=C bonds in the thiophene groups, and the C=N-C bonds in the imino groups, respectively [Figure S4b]. The N 1s signal exhibited three distinct peaks [Figure S4c], which correspond to the N atoms in the imino bonds, the C=N units in the triazine ring, and the dangling $-NH_2$ units, respectively.²¹ These peaks were located at 397.6, 398.2, and 401.8 eV. The S $2p_{3/2}$ and S $2p_{1/2}$ binding energies of S atoms in the thiophene groups were detected as signals at 163.3 and 164.6 eV, correspondingly [Figure S4d]. At 531.0 eV, the O 1s spectrum exhibited a prominent peak that was ascribed to the C==O



Figure 2. (a, d) XRD patterns of (a) TPBT-COF and (d) TPBTz-COF (black: experimentally observed), their simulated patterns calculated for Rietveld refinement (red: AA-stacking; blue: AB-stacking). (b) AA- and (c) AB-stacking models of TPBT-COF. (e) AA- and (f) AB-stacking models of TPBTz-COF.

on the anthraquinone moieties in TPBTz-COF. TPBT-COF and TPBTz-COF were successfully synthesized, as confirmed by the XPS spectra.

By utilizing TGA, the thermal stabilities of TPBT-COF and TPBTz-COF were evaluated. The thermal stabilities of TPBT-COF and TPBTz-COF were significantly greater than those of the monomers TPT-3NH₂, TPT-3CHO, BTT-3CHO, and BTz-2NH₂, as shown in Figure S5. At 10% weight loss (T_{d10}), the temperatures of TPBT-COF and TPBTz-COF were S61 and 453 °C, respectively. Significantly superior thermal stability characterized TPBT-COF as opposed to TPBTz-COF. Affecting the thermal stability of COFs are their substructures' symmetry and planarity.²² Thermal stability was significantly enhanced in TPBT-COF due to its exceptionally symmetrical and planar structure, which surpassed that of TPBTz-COF.

Figure S6 illustrates the UV–vis spectra of TPTP-COF, TPBT-COF, and TPBT2-COF in ethanol solution. Between 250 and 700 nm, the spectrum of TPTP-COF exhibits $\pi - \pi^*$ electronic transitions that are linked to a succession of distinctive vibration structures. The principal bands of absorbance appeared at wavelengths shorter than 500 nm. In contrast to the TPTP-COF, the TPBT-COF, which is

composed of benzotrithiophene and triazine units, exhibits a pronounced absorption band within the wavelength range of 400 to 850 nm. The visible absorption band is increased and conjugation is improved in the DA structure, which is advantageous for solar light absorption.³² A prominent absorption band was detected in the visible region for both TPBTz-COF and TPBT-COF. By integrating a benzobisthiazole unit as a conjugation bridge between triazine cores, the conjugation length and absorption intensity in the visible region were both increased.

3.2. Morphologies of the TPBT-COF and TPBTz-COF. By combining computational simulations with XRD, the crystal structures of TPBT-COF and TPBTz-COF were analyzed. The crystalline frameworks' periodic hexagonal lattices were validated by their XRD patterns (Figure 2). The crystal structure of TPBT-COF was identified in Figure 2a by a distinct diffraction peak at a value of 2θ of 4.62° , which corresponds to a reflection of magnitude 100. Additionally, there were three additional peaks at 8.11, 9.38, and 12.42°, which were subsequently attributed to reflections of magnitudes 110, 200, and 210, respectively.^{33,34} The marginally broad peak observed at a value of 2θ of 25.4° is a result of the (001) reflection introduced by π -stacking among the COF layers. Additionally, peaks at values 2θ of 3.22, 4.58, 6.48, 7.26, and 25.12° were observed in the XRD pattern of TPBTz-COF [Figure 2d]. These peaks correspond to the (100), (110), (200), (210), and (001) reflections, respectively. Furthermore, the average *d*-spacings among the 100 planes (d_{100}) and the interlayer distances between the 2D sheets of the planes were computed utilizing the Bragg equation:

$$n\lambda = 2d\,\sin\theta$$

where λ represents the wavelength of the incident waves (in this case, $\lambda = 0.154$ nm) and n is an integer (in this case, n =1). The d_{100} values for TPBT-COF and TPBTz-COF were 1.91 and 1.92 nm, while the corresponding interlayer distances were 3.50 and 3.54 Å. In addition, we conducted theoretical simulations of the crystal structure of the COFs utilizing the Materials Studio software. The simulated XRD diffraction images of TPBT-COF and TPBTz-COF are illustrated in Figure 2a,d, respectively. In addition, the simulated crystal structures of TPBT-COF for AA-stacking and AB-stacking models are presented in Figure 2b,c, while they are illustrated as TPBTz-COF in Figure 2e,f. The experimental and theoretical XRD reflections for TPBT-COF exhibited a strong correspondence, as demonstrated by the structural simulations of the AA-eclipsed layer stacking mode [Figure 2a]. The hexagonal structure of the P6/m space group was presented by the simulated AA-stacking (eclipsed) model for TPBT-COF. The unit cell parameters were as follows: a = b = 21.98 Å; c =3.49 Å; $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$ [Figure 2b]. Using AA-stacking, the simulated pore size of TPBT-COF was 2.11 nm. In contrast, the theoretical pattern [Figure 2d] was nearly identical to the experimental XRD reflections of TPBTz-COF, as demonstrated by the structural simulations of the ABstaggered layer stacking mode. The AB-stacking (staggered) model yielded the subsequent calculated parameters for the TPBTz-COF unit cell: a = b = 43.08 Å; c = 3.54 Å; $\alpha = \beta =$ 90°; $\gamma = 120^{\circ}$ [Figure 2f]. Based on the simulated pore size of 4.46 nm for TPBTz-COF with AA-stacking, its pore size would be less than 4.46 nm with AB-stacking. The simulated data and experimental XRD diffraction images confirmed that TPBT-COF had crystalline frameworks of the AB-stacking variety and hexagonal lattices. In contrast, TPBTz-COF had crystalline frameworks of the AB-stacking variety. AA-stacking crystalline framework of TPBT-COF was produced by the higher symmetry and planarity of the monomers TPT-3CHO and BTz-2NH₂. Conversely, the AB-stacking and reduced symmetry of TPBTz-COF were outcomes of the BTz-2NH₂based long bridge connecting the triazine units.

The characterization of the nanostructures of TPTP-COF, TPBT-COF and TPBTz-COF was performed using SEM images (Figure 3). The SEM image of TPTP-COF [Figure 3a] shows that microspheres with an average particle size of 0.5-1 μ m are distributed on the surface of the bulk material. The TEM image shows that the TPTP-COF features granular nanoparticles with an average diameter of 25 nm [Figure 3b]. The SEM image demonstrated that the TPBT-COF underwent aggregation of nanoparticles, resulting in the formation of a chrysanthemum-like structure [Figure 3c]. The TEM analysis yielded additional information regarding the nanostructure resembling petals of the TPBT-COF [Figure 3d]. TPBTz-COF was observed to be rod-shaped in the SEM image, with diameters ranging from 50 to 500 nm and ultralong lengths reaching several micrometers [Figure 3e]. The structures of the TPBTz-COF were illustrated in greater detail by HRTEM



Figure 3. SEM ((a), (c), (e)) and TEM ((b), (d), (f)) images of (a), (b) TPTP-COF; (c), (d) TPBT-COF; (e), (f) TPBTz-COF.

[Figure 3f]. Apart from that, the SEM images of the TPTP-COF, TPBT-COF, and TPBTz-COF samples after ultrasonic treatment are shown in Figure 4. The particle sizes of the COFs were much smaller than those of the pristine COF samples. The particle sizes of the TPTP-COF, TPBT-COF, and TPBTz-COF samples were approximately 205.8, 396.3, and 149.1 nm, respectively.

3.3. BET Surface Areas and Pore Sizes of the TPBT-COF and TPBTz-COF. By analyzing N_2 adsorption-desorption isotherms recorded at 77 K (Figure S7), we assessed the porosities of the COFs. The TPTP-COF has a specific surface area of 426.6 $\text{m}^2 \text{g}^{-1}$ and a pore size of 3.86 nm, as reported in reference.²² The sorption curve of TPBT-COF revealed type I isothermal behavior, characteristic of a microporous polymer [Figure S7a].³⁵ The specific surface area of TPBT-COF was measured at 1163.5 m² g⁻¹ using the Brunauer–Emmett–Teller (BET) method. On the other hand, TPBTz-COF displayed a standard II isotherm, suggesting a microporous structure [Figure S7b].³⁶ The specific surface area of TPBTz-COF was measured at 20.34 m² g⁻¹, which was significantly less than that of TPBT-COF. The behavior was a result of TPBT-COF being created from TPT-3CHO and the symmetrical and planar TPT-3NH₂, while TPBTz-COF was formed from the reaction of TPT-3CHO with the relatively long bridge of BTz-2NH₂. According to Figure S7c, the pore widths of TPBT-COF were mostly around 1.30 nm, slightly smaller than the simulated value for the AA-eclipsed stacking model. The smaller pore size of TPBT-COF results from the buildup of particles. At the same time, the long bridge made of BTz-2NH₂ between triazine units leads to the larger pore size (6.30 nm) of TPBTz-COF [Figure S7d]. The TPBTz-COF pore size was a bit larger than the simulated value of 4.46 nm



Figure 4. SEM images of the (a) TPTP-COF, (b) TPBT-COF, and (c) TPBTz-COF samples (prepared by subjecting the COF solution to ultrasonic treatment at room temperature for 2 h).

for the AA-eclipsed stacking model. Indicating the existence of a crystal defect within the TPBTz-COF.³⁷

3.4. Particle Size Distribution of the COFs in MAI/Pbl₂ Precursor Solution. Figure S8 displays the particle size distribution of the COFs in DMF/DMSO (4/1, v/v). According to the results, the particle size of the COFs in the solvent dispersion was significantly smaller compared to the COFs in the solid state (see Figure 3). Intense connections among the COF caused the COF' to clump together and form large particles in the solid state. When using DMF/DMSO solvent, the TPBTz-COF displayed a significantly smaller average particle size compared to the TPTP-COF and TPBT-COF. Furthermore, the TPBTz-COF exhibited a significantly narrower particle size distribution compared to the TPTP-COF and TPBT-COF. TPBT-COF exhibits the largest average particle size and the broadest particle size distribution. In addition, Figure S9 shows the particle size distribution of the COFs (10 wt %) in the MAI/PbI₂ solution. In this solution, the particle size distribution of TPBTz-COF was narrower compared to that of TPTP-COF and TPBT-COF. However, the particle size distributions of the COFs in the MAI/PbI₂ solution were broader than those in the DMF/DMSO solvent. By incorporating the same weight content of the COF in the MAPbI₃ layer, the TPBTz-COF with a smaller particle size leads to increased interactions at the COF/MAPbI₃ interface. The size and distribution of particles in the COF significantly impact the structure and photoelectronic characteristics of the COF-infused MAPbI₃ layer.

3.5. SEM Images of the COF-Incorporated Perovskite Films. Examining the impact of the COF as an additive on the crystallization of perovskite films involved using SEM to analyze the morphologies and film qualities of MAPbI₃ on the NiO_r layer. This helped in identifying the best processing conditions for PVSC preparation. Displayed in Figure 5a-j are the top-view SEM images of the COF integrated MAPbI₃ films deposited on the NiO_x layer. As depicted in Figure 5b,c,d, the topographic image illustrates that the crystal grains of the TPTP-COF-incorporated MAPbI₃ layer remained largely unchanged in comparison to the original MAPbI₃ layer. However, the crystal grain sizes of the TPTP-6 based MAPbI₃ layer were slightly larger compared to those of the TPTP-3 and TPTP-10 based MAPbI₃ layers. Moreover, the crystal grain sizes of the TPBT-COF based MAPbI₃ layer were smaller compared to the pristine and TPTP-COF based MAPbI₃ layers [Figure 5e,f,g]. The electro-pair in the sulfur atoms of the benzotrithiophene unit in TPBT-COF interacts with the nitrogen atoms of MAI, leading to a reduction in the crystal defects of MAPbI₃.³⁸ However, the larger particle size of TPBT-COF in the precursor solution of the MAPbI₃ would hinder the crystal growth of the perovskite [Figure 4b]. In addition, the crystal grain sizes of the TPBTz-COF-based MAPbI₃ layer were larger compared to the pristine, TPTP-



Figure 5. Topographic SEM images of (a) pristine, (b) TPTP-3-, (c) TPTP-6-, (d) TPTP-10-, (e) TPBT-3-, (f) TPBT-6-, (g) TPBT-10-, (h) TPBTz-3-, (i) TPBTz-6-, and (j) TPBTz-10-incorporated perovskite films, recorded after they had been subjected to annealing at 100 °C for 10 min.

COF, and TPBT-COF-incorporated MAPbI₃ layers as shown in Figure 5h,i,j. The TPBTz-COF based perovskite layer exhibited the largest crystal grain size, particularly in the TPBTz-6 perovskite film. Utilizing the smaller particle size of TPBTz-COF with a larger specific surface area in the precursor solution of the MAPbI₃ acted as a crystal growth template, resulting in a larger crystal grain size of the perovskite [Figure 5i]. In addition, the specific surface area of the COF does not appear to be a critical factor in the crystal growth of the perovskite film. The specific surface area of TPBTz-COF was much smaller than that of TPTP-COF and TPBT-COF, yet the crystal size of the TPBTz-COF doped MAPbI₃ layer was larger than those of the TPTP-COF and TPBT-COF doped MAPbI₃ layers.

Furthermore, Figures 6a-j display the cross-sectional SEM images of the COF-incorporated MAPbI₃ films deposited on



Figure 6. Cross-sectional SEM images of (a) pristine, (b) TPTP-3–, (c) TPTP-6–, (d) TPTP-10–, (e) TPBT-3–, (f) TPBT-6–, (g) TPBT-10–, (h) TPBTz-3–, (i) TPBTz-6–, and (j) TPBTz-10– based perovskite films, recorded after they had been subjected to annealing at 100 $^{\circ}$ C for 10 min.

the NiO_x layer. After the addition of COF in the MAPbI₃ layers, the result showed an increase in the thickness of the MAPbI₃ layer. It suggests that the COF frameworks facilitated the perovskite layer's crystal growth. Increasing the thickness of the COF/MAPbI₃ layer enhanced the absorption of solar light. Yet, a greater amount of the COF did not support the crystal growth of the perovskite layer. An excess amount of the COF additive increased the number of nucleation sites for

crystal formation and suppressed the crystal size and thickness of the perovskite layer. Therefore, the thickness of the COF/ MAPbI₃ layer decreased when an excess amount of COF was added to the TPTP-10, TPBT-10, and TPBTz-10 samples (Figure 6d,g,j). In addition, the cross-sectional SEM images showed that the TPBTz-3 and TPBTz-6 samples had larger crystal grain sizes compared to the pristine and other COFincorporated MAPbI₃ layers.

We used AFM microscopy to confirm the effects of adding COFs (TPTP-COF, TPBT-COF, and TPBTz-COF) on the morphologies of perovskite films. Figure S10 displays AFM images of the TPTP-COF/MAPbI₃, TPBT-COF/MAPbI₃, and TPBTz-COF/MAPbI₃ composite films, respectively, after annealing at 100 °C for 10 min. Table S1 summarizes the surface roughness values of the COF-incorporated MAPbI₃ layers. The AFM images indicate that the surface roughness values of the COF/MAPbI₃ composite films are slightly lower than those of the pristine MAPbI₃ film. Moreover, the surface roughness values of the TPBT-COF/MAPbI₃ and TPBTz-COF/MAPbI₃ composite films are smaller than those of the TPTP-COF/MAPbI₃ composite films. The decrease in surface roughness of the COF/MAPbI₃-based composite films indicates that the presence of the COF leads to defect passivation.39

3.6. XRD and XPS Spectra of the COF-Incorporated Perovskite Films. Analyzing the crystal structures of the COF-incorporated perovskite films deposited on the NiO_x layers was done using XRD. The XRD patterns of the TPTP-COF, TPBT-COF, and TPBTz-COF-incorporated MAPbI₃ films formed on the NiO_x layers showed the typical diffraction peaks of solution-processed MAPbI₃ perovskites, with characteristic peaks at 14.1, 28.4, and 43.08° corresponding to the (110), (220), and (330) phases, respectively [Figures 7a and S11]. Indications from the signals pointed to the creation of tetragonal perovskite structures with lattice constants a and b both measuring 8.883 Å and c measuring 12.677 Å. The (110) peak intensities of the TPTP-COF, TPBT-COF, and TPBTz-COF-incorporated MAPbI₃ films on NiO_x layers were greater than those of the pristine MAPbI₃ sample [Figure 7a]. In the MAPbI₃ films with TPTP-COF incorporation, the (110)peak showed the highest intensity in the TPTP-6 sample [Figure S11a]. The diffraction peak intensity of the MAPbI₃ film decreased with the increased TPTP-COF (TPTP-10) content in the perovskite layer. Moreover, the (220) and (330) peak intensities were not increased for the TPTP-COF integrated MAPbI₃ films, suggesting that the TPTP-COF integrated perovskite film has enhanced crystalline quality with a favored orientation.⁴⁰ When incorporating TPBT-COF into MAPbI₃ films, the intensities of the (110) peaks increased as the TPBT-COF content was raised [see Figure S11b]. The sample based on TPBT-6 showed the highest intensity of the (110) peak. When comparing the (110) peak intensities, it was found that they were not higher in the TPBT-COFincorporated MAPbI3 films compared to the TPTP-COFincorporated MAPbI₃ films. Moreover, the strength of the (110) peak showed an increase as the TPBTz-COF incorporation content in the MAPbI₃ film increased [Figure S11c]. The (110) peak showed the highest intensity in the sample based on TPBTz-6. When comparing the TPBTz-6 based sample to the TPBTz-10 based sample, it was observed that the intensity of the (110) peak was slightly reduced. At the same time, the intensities of the (220) and (330) peaks remained unchanged in the TPBTz-COF-incorporated



Figure 7. (a) XRD patterns and (b) UV-vis spectra of the TPTP-6, TPBT-6, and TPBTz-6 based perovskite films deposited on NiO_x layers, recorded after they had been subjected to annealing at 100 °C for 10 min; (c) PL spectra and (d) TRPL spectra of the TPTP-6, TPBT-6, and TPBTz-6 based perovskite films deposited on FTO coated glass, recorded after they had been subjected to annealing at 100 °C for 10 min.

MAPbI₃ films. Figure 7a illustrates that when the same content is added, the TPBTz-6 sample exhibits a higher diffraction intensity of the (110) peak compared to the TPTP-6 and TPBT-6 samples. The TPBTz-COF's smaller average particle size and larger specific surface area enhanced crystal growth and defect passivation in the MAPbI₃ layer.

The characteristic peaks of Pb valence electrons in Pb $4f_{7/2}$ and Pb $4f_{5/2}$ of the TPTP-6, TPBT-6, and TPBTz-6 films exhibit obvious shifts toward higher binding energies compared to the pristine MAPbI₃ film (Figure S12). These results indicate the existence of a chemical interaction between the COF and Pb(II) in the perovskite crystal. Compared to the nitrogen-containing TPTP-COF additive, a larger binding energy shift was observed in the MAPbI₃ film with the nitrogen- and sulfur-containing TPBT-COF and TPBTz-COF additives, especially with the TPBTz-COF additive. The larger shift was attributed to the strong interactions between the Pb²⁺ ions in the perovskite and the sulfur atoms in TPBT-COF and TPBTz-COF. The lone electron pairs in the sulfur and nitrogen atoms of benzobisthiazole are favorable for improving defect passivation in the perovskite layer.

3.7. Optical and Photophysical Properties of the COF-Incorporated Perovskite Films. Examining the UVvis spectra of the COF-incorporated MAPbI₃ layers deposited on the NiO_x layers revealed the additive effect of the COF on the optical properties of the perovskite films [Figures 7b and

S13]. When looking at the pristine MAPbI₃ film, it is clear that the TPTP-COF, TPBT-COF, and TPBTz-COF with incorporated MAPbI₃ films have a much stronger absorption across the entire spectral range. The enhancement of the absorption intensity is attributed to the improved morphology and crystallinity in the perovskite film.⁴⁰ The absorption intensities of TPBT-COF and TPBTz-COF were significantly higher than those of TPTP-COF (refer to Figure S6), whereas the absorption intensities of TPTP-COF, TPBT-COF, and TPBTz-COF-incorporated perovskite films were nearly identical in the wavelength range from 500 to 750 nm (see Figures 7b and S13). This indicates that a low addition content of the COF resulted in minimal contribution to the absorption of the COF in the 500-750 nm wavelength range for the COF/ MAPbI₃-based perovskite layer. Between 400 and 500 nm, the TABTz-COF-incorporated MAPbI₃ films showed stronger absorption compared to the TPTP-COF and TABT-COFincorporated MAPbI3 films. This is attributed to the larger crystal grain size and higher crystal intensity in the TABTz-COF-incorporated MAPbI₃ films. In addition, the absorption intensities of the TPTP-COF-incorporated MAPbI₃ films exceeded those of the TABT-COF-incorporated MAPbI₃ films due to the superior crystal quality of the former. Furthermore, Figure S13 illustrates the impact of the COF concentration on the absorption intensity of the MAPbI₃ film. The TPTP-6 samples exhibited higher absorption intensities

(a)

E/eV vs. vacuum

PCE (%)



0 0 500 550 600 650 700 750 400 450 800 200 300 400 700 800 350 0 100 500 600 Wavelength (nm) Time (hrs)

Figure 8. (a) Energy level diagram of $COF/MAPbI_3$ blend films.; (b) Current density-voltage characteristics of illuminated (AM 1.5G, 100 mW cm⁻²) PVSCs; (c) IPCE spectra of PVSCs, recorded under monochromatic irradiation; (d) storage stability of pristine MAPbI₃, TPTP-6, TPBT-6, and TPBTz-6 based PVSCs.

compared to the TPTP-3 and TPTP-10 samples. Similar observations were made with the TABT-COF and TABTz-COF integrated MAPbI₃ films.

Figures 7c and S14 show the PL spectra of the COFincorporated MAPbI₃ films deposited on the FTO glass. The peak wavelength of the perovskite films' photoluminescence was around 768 nm. The PL intensities of the TPTP-COF, TPBT-COF, and TPBTz-COF doped MAPbI₃ films were significantly greater compared to the original MAPbI₃ film. Based on the higher PL intensity, it indicates a lower presence of defects and a more crystalline structure in the perovskite.⁴¹⁻⁴³ Furthermore, in the same content of COF, the PL intensities of the TPBTz-COF-incorporated MAPbI₃ films exceeded those of the TPTP-COF and TPBT-COF based samples. The increased PL intensity of the COF-infused MAPbI₃ films indicates that adding COFs can help decrease defects in the layer and enhance radiative recombination.⁴¹ The PL intensities of the MAPbI₃ films with COF incorporation increased as the COF content was raised (Figure S14). However, the PL intensity decreased as more of the COF was added to the MAPbI₃ film.

Examining the TRPL spectra was done to investigate how carriers recombine in the MAPbI₃ films with COF incorporation [Figure 7d]. We calculated the carrier lifetime by analyzing the PL data using a biexponential decay model^{44,45}

$$I(t) = A \mathrm{e}^{-t/\tau_1} + B \mathrm{e}^{-t/\tau_2}$$

The formula provided involves exponential decay with constants *A*, *B*, τ_1 , and τ_2 representing different decay rates. Table S2 provides a summary of the fitting results for the TRPL spectra. In this case, we calculated the average lifetime by taking the average of the fast and slow decay constants, which were determined using the formula

$$\tau_{\rm avg} = (A\tau_1^2 + B\tau_2^2) / (A\tau_1 + B\tau_2)$$

The constant τ_1 is associated with defect recombination or interfacial charge transport from MAPbI₃ to the charge transport materials; τ_2 is linked to radiative recombination.⁴³ The lifetimes of the TPTP-COF, TPBT-COF, and TPBTz-COF–doped MAPbI₃ films were found to be longer compared to the pristine MAPbI₃ film. Furthermore, the TPBTz-6 sample had a significantly longer average lifetime compared to the TPTP-6 and TPBT-6 samples. The extended lifespan was due to the lower defect density, which inhibits the nonradiative recombination of photogenerated electron and hole in the COF-incorporated MAPbI₃ films.⁴⁰ The decrease in crystal defects in the MAPbI₃ film could be attributed to the effective passivation by the COF, particularly for the TPBTz-6 sample.⁴¹

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Exploring the energy band structures of the COF/MAPbI₃ blend films was done through UPS spectroscopy. In Figure S15a, you can see the UPS spectra for the cutoff region and the valence band boundary region of COF/MAPbI₃ blend films. The formulas for calculating the WF and VBM values of COF/ MAPbI₃ blend films are as follows: WF = $21.22 - E_{cutoff}$ and VBM = WF + E_{onset} where E_{cutoff} and E_{onset} are identified in Figure S15b,c, respectively.⁴⁶ By analyzing the UV-vis absorption spectra [Figure 7b], the energy band gaps (E_{σ}) of COF/MAPbI₃ blend films were determined. Through the combination of UV-vis absorption spectra's band gap, the CBM values of the COF/MAPbI₃ blend films were established. The UPS spectra were used to summarize the estimated energy level values of COF/MAPbI₃ blend films in Table S3. Furthermore. Shown in Figure 8a is the energy level diagram for COF/MAPbI₃ blend films. The outcome showed that the energy band gap of the MAPbI₃ film was altered due to the inclusion of the COF. The blend films showed higher VBM levels compared to the pristine MAPbI₃ film. The higher VBM level of the COF/MAPbI₃ blend film promotes efficient holetransport from the perovskite layer to the NiO_x layer, particularly for the TPBTz-6.

3.8. Charge Mobilities and PV Properties of PVSCs Fabricated from the COF-Incorporated Perovskite Layers. Measuring the hole and electron mobilities in the COF-incorporated MAPbI₃ layers was essential to explore the additive effects of the COF on the perovskite layers. Figure S16 illustrates the current density–voltage plots of the FTO/MAPbI₃:COF/Au hole-only device and the FTO/MAPbI₃:COF/PC₆₁BM/BCP/Ag electron-only device. In the space-charge limited current regime, the hole and electron mobilities (μ) of the perovskite were determined utilizing the following equation:

$$J = 9/8 \varepsilon_{\rm r} \varepsilon_{\rm o} \mu V^2 / L^3$$

where J denotes the current density, ε_{o} signifies the vacuum permittivity (8.854 \times 10⁻¹² F m⁻¹), $\varepsilon_{\rm r}$ represents the relative permittivity of MAPbI₃ (32), V signifies the base voltage, and L signifies the thickness of the MAPbI3 layer.47,48 The hole mobilities of the pristine MAPbI₃, TPTP-6-, TPBT-6-, and TPBTz-6-based hole-only devices were 1.24×10^{-3} , 1.86×10^{-3} , 1.77×10^{-3} , and 1.91×10^{-3} cm² V⁻¹ s⁻¹, respectively. In addition, the electron mobilities of the different devices were estimated as follows: 1.75 \times 10^{-3}, 3.45 \times 10^{-3}, 2.46 \times 10^{-3} , and $4.03 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the pristine MAPbI₃, TPTP-6-, TPBT-6-, and TPBTz-6-based electron-only devices, respectively. Consequently, the hole and electron mobilities in the COF-infused perovskite layers surpassed those of the original sample. On the other hand, the hole and electron mobilities of the TPBTz-6-based devices exceeded those of the TPTP-6- and TPBT-6-based hole-only devices. The hole and electron mobilities of the TPTP-6-based devices surpassed those of the TPBT-6-based devices, despite the TPBT having a DA conjugated structure. This is because the crystal quality of the TPTP-COF-incorporated MAPbI₃ layer was better than that of the one incorporated with TPBT-COF. The study found that the COF had a more positive impact on the hole and electron mobilities of the perovskite layer compared to the control sample. This was due to the improved morphology and higher crystal quality.

Figure 8b,c shows the photocurrent density-voltage plots and incident photon-to-current efficiency (IPCE) spectra of the PVSCs made from the TPTP-COF, TPBT-COF, and

TPBTz-COF with MAPbI₃ layers. Figure S17 also provides relevant information. Table S4 provides a summary of the statistical values for the PV properties of these PVSCs, such as their open-circuit voltages (V_{OC}) , short-circuit current densities (J_{SC}) , fill factors (FFs), and PCEs. The PVSC-I achieved a $V_{\rm OC}$ of 1.03 V, JSC of 22.85 mA cm⁻², FF of 71.6%, and a PCE of 16.85% using the control pristine MAPbI₃ layer. Compared to the original PVSC-I, the PV properties (I_{SC} , FF, and PCE) of the PVSCs with TPTP-COF, TPBT-COF, and TPBTz-COF showed significant improvement (PVSC-II-PVSC-XI). In addition, the IPCE spectra validated the increase in I_{SC} values of PVSCs made from the COF integrated MAPbI₃ layers [Figure 8c]. The IPCEs for the TPTP-6, TPBT-6, and TPBTz-6 derived PVSCs exceeded that of the PVSC I based on the pristine MAPbI₃ layer. The occurrence of optical interference results in ripple curves in the IPCE spectra for incident optical wavelengths larger than 500 nm.49,50 The interference peaks are strongly dependent on the thickness of the COF-incorporated perovskite film. Using the same components, the PV performance of PVSCs with TPBTz-COF was superior to those with TPTP-COF and TPBT-COF. The PV performance of the TPTP-COF-incorporated PVSCs (PVSC-II, PVSC-III, and PVSC-IV) outperformed those of the TPBT-COF-incorporated PVSCs (PVSC-V, PVSC-VI, and PVSC-VII). Nevertheless, the current density slightly increased as the voltage decreased from 0.7 to 0 V for the TPTP-6 based PVSC, which was attributed to the leakage current density of the cell (In Figure 8b).⁵¹ Moreover, the PV characteristics saw enhancement following the increase in COF content in the MAPbI₃ layer for the TPBTz-COF based PVSCs. The TPBTz-6 based PVSC IX demonstrated outstanding performance with a $V_{\rm OC}$ of 1.04 V, $J_{\rm SC}$ of 24.26 mA cm⁻², FF of 78.2%, and a PCE of 20.04%. The significant J_{SC} and FF values align with the increased crystal grain size, enhanced XRD diffraction intensity, improved UV-vis absorption, and higher charge mobility of the TPBTz-6 perovskite film. By incorporating the ideal amount of TPBTz-6 into the MAPbI₃ layer, it facilitated crystal growth and improved crystal quality of the perovskite layer. This resulted in effective charge separation and extraction as well as increased charge mobility. However, an excessive amount of the COF did not benefit the improvement of the PV performance of the PVSC. The PV properties of PVSC XI based on TPBTz-10 were slightly inferior to those of PVSC IX based on TPBTz-6. The additional content effects of TPTP-COF and TPBT-COF on the PV performance of MAPbI₃ based PVSCs are similar to TPBTz-COF based PVSCs. Additionally, a high efficiency of 20.04% from forward scanning and a comparable efficiency of 19.92% from reverse scanning were obtained for the TPBTz-6 based PVSC IX (Figure S18). The negligible hysteresis of the current density– voltage curve implies balanced charge transport at the NiO_x (or PC₆₁BM)/MAPbI₃ interface and good charge transport within the MAPbI₃ layer for PVSC IX.

Figure 8d displays the storage stabilities of the PVSCs (PVSC I, PVSC III, PVSC VI, and PVSC-IX) based on the Pristine MAPbI₃, TPTP-6, TPBT-6, and TPBTz-6, measured at 30 °C and 40% relative humidity. The PCE stability of the COF-based PVSCs outperformed that of the Pristine MAPbI₃ based PVSC I. Furthermore, the PCE stability of the PVSC IX based on TPBTz-6 outperformed that of the PVSCs TPTP-6 and TPBT-6 (PVSC-III and PVSC-VI). TPBTz-6 based PVSC IX demonstrated a lifetime exceeding 750 h without encapsulation. In addition, the TPTP-6-based PVSC-III

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exhibited superior stability compared to the TPBT-6 based PVSC-VI. Introducing the COF into the perovskite layer enhances crystal growth and effectively passivates crystal defects to stabilize the perovskite crystal structures.

4. CONCLUSIONS

Developed in this study are triazine-based COFs (TPTP-COF, TPBT-COF, and TPBTz-COF) with highly porous characteristics, large specific surface areas, high crystallinity, and a welldefined conjugated structure. The COFs' frameworks in the MAPbI₃ layer can serve as a template for the crystal growth of perovskite, enhancing the crystal film quality, stability, and repairing crystal defects in perovskite materials. The TPBTz-COF exhibited a higher conjugation intensity compared to the TPTP-COF and TPBT-COF. The TPBTz-COF with enhanced conjugation intensity demonstrated superior charge transfer capability within the COF structure. In solution state, the average particle sizes of the TPBTz-COF were significantly smaller compared to the TPTP-COF and TPBT-COF. Using a precursor solution with the smallest particle size of TPBTz-COF leads to increased interactions at the interface between COF and MAPbI₃ in the perovskite layer. The crystal grain size, PL intensity, carrier lifetime, and charge mobility of TPBTz-COF-incorporated MAPbI₃ layer exceeded those of the TPTP-COF and TPBT-COF-incorporated MAPbI₃ layer. The charges generated in the MAPbI₃ layer can be efficiently separated and transferred due to the conjugated framework of the COF. This framework effectively inhibits charge recombination and boosts charge separation efficiency. The PV performance and stability of the TPBTz-COF-incorporated PVSCs outperformed the TPTP-COF and TPBT-COFincorporated PVSCs. The additive effect of COF was significantly influenced by the conjugation structure of the COF and the particle size in the MAPbI₃ precursor solution of the COF.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.4c04301.

Synthesis route of the TPBT-COF and TPBTz-COF; FTIR, ¹³C NMR, XPS, and UV–vis spectra of the COFs; N₂ adsorption–desorption isotherms; XRD patterns, UV–vis absorption, PL spectra, and UPS spectra of the COF-incorporated MAPbI₃ films; fitted parameters of the TRPL spectra; energy levels of the COF/MAPbI₃ blend films; hole- and electron mobilities; current density–voltage curve of the COF-based PVSCs; PV parameters of PVSCs (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the National Science and Technology Council (NSTC) of Taiwan (grant no. NSTC 112-2221-E-005-004) for financial support.

REFERENCES

(1) Suresh Kumar, N.; Naidu, K. C. B. A review on perovskite solar cells (PSCs), materials and applications. *J. Materiomics* **2021**, *7*, 940–956.

(2) Chen, J.; Dong, H.; Li, J.; Zhu, X.; Xu, J.; Pan, F.; Xu, R.; Xi, J.; Jiao, B.; Hou, X.; Ng, K. W.; Wang, S. P.; Wu, Z. Solar cell efficiency exceeding 25% through Rb-based perovskitoid scaffold stabilizing the buried perovskite surface. ACS Energy Lett. 2022, 7, 3685–3694.

(3) Gu, N.; Song, L.; Zhang, P.; Feng, Y.; Du, P.; Zhu, Y.; Ning, L.; Sun, Z.; Jiang, H.; Xiong, J. ETL-free perovskite solar cells with an efficiency of 19.81% in ppen air. ACS Sustainable Chem. Eng. 2023, 11, 13646–13655.

(4) Jiang, Q.; Tong, J.; Xian, Y.; Kerner, R. A.; Dunfield, S. P.; Xiao, C.; Scheidt, R. A.; Kuciauskas, D.; Wang, X.; Hautzinger, M. P.; Tirawat, R.; Beard, M. C.; Fenning, D. P.; Berry, J. J.; Larson, B. W.; Yan, Y.; Zhu, K. Surface reaction for efficient and stable inverted perovskite solar cells. *Nature* **2022**, *611*, 278–283.

(5) Cai, F.; Yan, Y.; Yao, J.; Wang, P.; Wang, H.; Gurney, R. S.; Liu, D.; Wang, T. Ionic additive engineering toward high-efficiency perovskite solar cells with reduced grain boundaries and trap density. *Adv. Funct. Mater.* **2018**, *28*, No. 1801985.

(6) Chu, H. Y.; Hong, J. Y.; Huang, C. F.; Wu, J. Y.; Wang, T. L.; Wu, T. M.; Lee, R. H. Enhanced photovoltaic properties of perovskite solar cells by the addition of cellulose derivatives to $MAPbI_3$ based photoactive layer. *Cellulose* **2019**, *26*, 9229–9239.

(7) Zheng, X.; Chen, B.; Dai, J.; Fang, Y.; Bai, Y.; Lin, Y.; Wei, H.; Zeng, X. C.; Huang, J. Defect passivation in hybrid perovskite solar cells using quaternary ammonium halide anions and cations. *Nat. Energy* **2017**, *2*, No. 17102.

(8) Chen, B.; Rudd, P. N.; Yang, S.; Yuan, Y.; Huang, J. Imperfections and their passivation in halide perovskite solar cell. *Chem. Soc. Rev.* **2019**, *48*, 3842–3867.

(9) Fu, L.; Li, H.; Wang, L.; Yin, R.; Li, B.; Yin, L. Defect passivation strategies in perovskites for an enhanced photovoltaic performance. *Energy Environ. Sci.* **2020**, *13*, 4017–4056.

(10) Chen, H. C.; Lan, J. M.; Hsu, H. L.; Li, C. W.; Shieh, T. S.; Wong, K. T.; Chen, C. P. Synergistic improvements in the performance and stability of inverted planar MAPbI₃-based perovskite solar cells incorporating benzylammonium halide salt additives. *Mater. Chem. Front.* **2021**, *5*, 3378–3387.

(11) Zhang, H.; Pfeifer, L.; Zakeeruddin, S. M.; Chu, J.; Grätzel, M. Tailoring passivators for highly efficient and stable perovskite solar cells. *Nat. Rev. Chem.* **2023**, *7*, 632–652.

(12) Xu, X.; Sun, Y.; He, D.; Liang; Liu, G.; Xu, S.; Li, Z.; Zhu, L.; Pan, X. Grain size control for high-performance formamidinium-based perovskite solar cells via suppressing heterogenous nucleation. *J. Mater. Chem. C* **2021**, *9*, 208–213.

(13) Zhang, Y. W.; Cheng, P. P.; Tan, W. Y.; Min, Y. Balance the thickness, transparency and stability of semi-transparent perovskite solar cells by solvent engineering and using a bifunctional additive. *Appl. Surf. Sci.* **2021**, *537*, No. 147908.

(14) Tailor, N. K.; Abdi-Jalebi, M.; Jalebi, M. A.; Gupta, V. H.; Hu; Dar, M. I.; Li, G. Recent progress in morphology optimization in perovskite solar cell. *J. Mater. Chem. A* **2020**, *8*, 21356–21386.

(15) Zhang, Z.; Qiao, L.; Meng, K.; Long, R.; Chen, G.; Gao, P. Rationalization of passivation strategies toward high-performance perovskite solar cells. *Chem. Soc. Rev.* **2023**, *52*, 163–195.

(16) Wu, Z.; Bi, E.; Ono, L. K.; Li, D.; Bakr, O. M.; Yan, Y.; Qi, Y. Passivation strategies for enhancing device performance of perovskite solar cells. *Nano Energy* **2023**, *115*, No. 108731.

(17) Zhang, H.; Ji, X.; Yao, H.; Fan, Q.; Yu, B.; Li, J. Review on efficiency improvement effort of perovskite solar cell. *Sol. Energy* **2022**, 233, 421–434.

(18) Chang, S. Y.; Elewa, A. M.; Mohamed, M. G.; Mekhemer, I. M. A.; Samy, M. M.; Zhang, K.; Chou, H. H.; Kuo, S. W. Rational design and synthesis of bifunctional Dibenzo[g,p]chrysene-based conjugated microporous polymers for energy storage and visible light-driven photocatalytic hydrogen evolution. *Mater. Today Chem.* **2023**, *33*, No. 101680.

(19) Geng, K.; He, T.; Liu, R.; Dalapati, S.; Tan, K. T.; Li, Z.; Tao, S.; Gong, Y.; Jiang, Q.; Jiang, D. Covalent organic frameworks: design, synthesis, and functions. *Chem. Rev.* **2020**, *120*, 8814–8933.

(20) Abuzeid, H. R.; EL-Mahdy, A. F. M.; Kuo, S. W. Covalent organic frameworks: Design principles, synthetic strategies, and diverse applications. *Giant* **2021**, *6*, No. 100054.

(21) Yang, Y.; Niu, H.; Xu, L.; Zhang, H.; Cai, Y. Triazine functionalized fully conjugated covalent organic framework for efficient photocatalysis. *Appl. Catal. B: Environ.* **2020**, *269*, No. 118799.

(22) Yang, H. C.; Chen, Y. Y.; Suen, S. Y.; Lee, R. H. Triazine based covalent organic framework/carbon nanotube fiber nanocomposites for high-performance supercapacitor electrodes. *Polymer* **2023**, *273*, No. 125853.

(23) Yao, L.; Zhang, Y.; Wang, H. X.; Guo, Y.; Zhuang, Z. M.; Wen, W.; Zhang, X.; Wang, S. An energy and charge transfer synergetic donor-acceptor heterostructure 2D-COF in photovoltaics. *J. Mater. Chem. A* **2020**, *8*, 8518–8526.

(24) Li, Z.; Han, S.; Li, C.; Shao, P.; Xia, H.; Li, H.; Chen, X.; Feng, X.; Liu, X. Screening metal-free photocatalysts from isomorphic covalent organic frameworks for the C3 functionalization of indoles. *J. Mater. Chem. A* **2020**, *8*, 8706.

(25) Wu, C.; Liu, Y.; Liu, H.; Duan, C.; Pan, Q.; Zhu, J.; Hu, F.; Ma, X.; Jiu, T.; Li, Z.; Zhao, Y. Highly conjugated three-dimensional

covalent organic frameworks based on spirobifluorene for perovskite solar cell enhancement. J. Am. Chem. Soc. **2018**, 140, 10016–10024. (26) Li, Z.; Zhang, Z.; Nie, R.; Li, C.; Sun, Q.; Shi, W.; Chu, W.; Long, Y.; Li, H.; Liu, X. Construction of stable donor–acceptor type covalent organic frameworks as functional platform for effective perovskite solar cell enhancement. Adv. Funct. Mater. **2022**, 32, No. 2112553.

(27) Liu, F.; He, Y.; Liu, X.; Wang, Z.; Liu, H. L.; Zhu, X.; Hou, C. C.; Weng, Y.; Zhang, Q.; Chen, Y. Regulating excitonic effects in covalent organic frameworks to promote free charge carrier generation. *ACS Catal.* **2022**, *12*, 9494–9502.

(28) Mohamed, M. G.; Lee, C. C.; EL-Mahdy, A. F. M.; Luder, J.; Yu, M. H.; Li, Z.; Zhu, Z.; Chueh, C. C.; Kuo, S. W. Exploitation of two-dimensional conjugated covalent organic frameworks based on tetraphenylethylene with bicarbazole and pyrene units and applications in perovskite solar cells. *J. Mater. Chem. A* **2020**, *8*, 11448– 11459.

(29) He, J.; Liu, H.; Zhang, F.; Li, X.; Wang, S. In situ synthesized 2D covalent Organic framework nanosheets induce growth of highquality perovskite film for efficient and stable solar cells. *Adv. Funct. Mater.* **2022**, *32*, No. 2110030.

(30) Huang, Y. J.; Cai, C. E.; Feng, Y. C.; Liu, B. T.; Lee, R. H. Water-soluble cationic copolyacrylamides modifying NiOx for high photovoltaic performance inverted perovskite solar cells. *ACS Appl. Polym. Mater.* **2023**, *5*, 8949–8959.

(31) Li, L.; Lu, F.; Xue, R.; Ma, B.; Li, Q.; Wu, N.; Liu, H.; Yao, W.; Guo, H.; Yang, W. Ultrastable triazine-based covalent organic framework with an interlayer hydrogen bonding for supercapacitor applications. *ACS Appl. Mater. Interfaces.* **2019**, *11*, 26355–26363.

(32) Kashiki, T.; Kohara, M.; Osaka, I.; Miyazaki, E.; Takimiya, K. Synthesis and Characterization of Benzo[1,2-b:3,4-b':5,6-b"]-trithiophene (BTT) Oligomers. J. Org. Chem. 2011, 76, 4061–4070.

(33) Xue, Q.; Hu, Z.; Sun, C.; Chen, Z.; Huang, F.; Yip, H. L.; Cao, Y. Metallohalide perovskite-polymer composite film for hybrid planar heterojunction solar cells. *RSC Adv.* **2015**, *5*, 775–783.

(34) Song, Z.; Watthage, S. C.; Phillips, A. B.; Tompkins, B. L.; Ellingson, R. J.; Heben, M. J. Impact of processing temperature and composition on the formation of methylammonium lead iodide perovskites. *Chem. Mater.* **2015**, *27*, 4612–4619.

(35) El-Mahdy, A. F.; Kuo, C. H.; Alshehri, A.; Young, C.; Yamauchi, Y.; Kim, J.; Kuo, S. W. Strategic design of triphenylamineand triphenyltriazine-based two-dimensional covalent organic frameworks for CO₂ uptake and energy storage. *J. Mater. Chem. A* **2018**, *6*, 19532–19541.

(36) Zhang, Z.; Nguyen, H.; Miller, S. A.; Cohen, S. M. PolyMOFs: A class of interconvertible polymer-metal organic-framework hybrid materials. *Angew. Chem., Int. Ed.* **2015**, *54*, 6152–6157.

(37) Park, J. H.; Lee, C. H.; Ju, J. M.; Lee, J. H.; Seol, J.; Lee, S. U.; Kim, J. H. Bifunctional covalent organic framework-derived electrocatalysts with modulated *p*-band centers for rechargeable Zn-air batteries. *Adv. Funct. Mater.* **2021**, *31*, No. 2101727.

(38) Chen, N. Y.; Yue, Q.; Liu, W.; Zhang, H. L.; Zhu, X. A benzo[1,2-d:4,5-d']bisthiazole-based wide bandgap copolymer semiconductor for efficient fullerene-free organic solar cells with a small energy loss of 0.50 eV. J. Mater. Chem. A **2019**, *7*, 5234–5238.

(39) Du, C. S.; Ho, I. H.; Huang, Y. J.; Lee, R. H. Quaternary ammonium halide-containing cellulose derivatives for defect passivation in MAPbI₃-based perovskite solar cells. *Sustainable Energy Fuels* **2022**, *6*, 3349–3362.

(40) Yang, Y.; Han, D. W.; Yang, Y.; Yi, S. W.; Yuan, Q.; Zhou, D. Y.; Feng, L. Redox-inactive samarium (III) acetylacetonate as dopant enabling cation substitution and interfacial passivation for efficient and stable CsPbI₂Br perovskite solar cells. *APL Mater.* **2020**, *8*, No. 071102.

(41) He, J.; Liu, H.; Zhang, F.; Li, X.; Wang, S. In situ synthesized 2D covalent organic framework nanosheets induce growth of highquality perovskite film for efficient and stable solar cells. *Adv. Funct. Mater.* **2022**, *32*, No. 2110030. (42) Shi, Z. E.; Long, J. Y.; Li, C. W.; Hsieh, S. Y.; Hsiao, Y.; Chen, S. C. P.; Yu, Y. H. A multifunctional ligand for defect passivation of perovskite film realizes air-stable perovskite solar cells with efficiencies exceeding 20%. *Sustainable Energy Fuels* **2022**, *6*, 1950–1958.

(43) Choi, M. J.; Lee, Y. S.; Cho, I. H.; Kim, S. S.; Kim, D. H.; Kwon, S. N.; Na, S. I. Functional additives for high-performance inverted planar perovskite solar cells with exceeding 20% efficiency: selective complexation of organic cations in precursors. *Nano Energy* 2020, *71*, No. 104639.

(44) Dubey, A.; Adhikari, N.; Mabrouk, S.; Wu, F.; Chen, K.; Yang, S.; Qiao, Q. A strategic review on processing routes towards highly efficient perovskite solar cells. *J. Mater. Chem. A* **2018**, *6*, 2406–2431.

(45) Li, X.; Liu, X.; Wang, X.; Zhao, L.; Jiu, T.; Fang, J. Polyelectrolyte based hole-transporting materials for high performance solution processed planar perovskite solar cells. *J. Mater. Chem. A* **2015**, *3*, 15024–15029.

(46) Liu, B. T.; Zhang, Y. Z.; Zuo, Y. Y.; Rachmawati, D. Passivation and energy-level change of the SnO_2 electron transport layer by reactive titania for perovskite solar cells. *J. Alloys Compd.* **2022**, *929*, No. 167349.

(47) Rose, A. A space-charge-limited currents in solids. *Phys. Rev.* **1955**, 97, 1538–1544.

(48) Targhi, F. F.; Jalili, Y. S.; Kanjouri, F. MAPbI₃ and FAPbI₃ perovskites as solar cells: case study on structural, electrical and optical properties. *Results Phys.* **2018**, *10*, 616–627.

(49) Behrouznejad, F.; Li, X.; Umar, A. A.; Zhang, X.; Khosroshahi, R.; Saad, S. K. M.; Ahmed, I.; Taghavinia, N.; Zhan, Y. The fingerprint of charge transport mechanisms on the incident photon-to-current conversion efficiency spectra of perovskite solar cells. *Sol. Energy Mater. Sol. Cells* **2023**, *253*, No. 112234.

(50) Lin, Q.; Armin, A.; Nagiri, R. C. R.; Burn, P. L.; Meredith, P. Electro-optics of perovskite solar cells. *Nat. Photonics* **2015**, *9*, 106–112.

(51) Kim, D. I.; Lee, J. W.; Jeong, R. H.; Boo, J. H. A high-efficiency and stable perovskite solar cell fabricated in ambient air using a polyaniline passivation layer. *Sci. Rep.* **2022**, *12*, No. 697.