In Situ Surface Fluorination of TiO₂ Nanocrystals Reinforces Interface Binding of Perovskite Layer for Highly Efficient Solar Cells with Dramatically Enhanced Ultraviolet-Light Stability

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Low-temperature solution-processed TiO₂ nanocrystals (LT-TiO₂) have been extensively applied as electron transport layer (ETL) of perovskite solar cells (PSCs). However, the low electron mobility, high density of electronic trap states, and considerable photocatalytic activity of TiO₂ result in undesirable charge recombination at the ETL/perovskite interface and notorious instability of PSCs under ultraviolet (UV) light. Herein, LT-TiO₂ nanocrystals are in situ fluorinated via a simple nonhydrolytic method, affording formation of Ti—F bonds, and consequently increase electron mobility, decrease density of electronic trap states, and inhibit photocatalytic activity. Upon applying fluorinated TiO₂ nanocrystals (F-TiO₂) as ETL, regular-structure planar heterojunction PSC (PHJ-PSC) achieves a champion power conversion efficiency (PCE) of 22.68%, which is among the highest PCEs for PHJ-PSCs based on LT-TiO₂ ETLs. Flexible PHJ-PSC devices based on F-TiO₂ ETL exhibit the best PCE of 18.26%, which is the highest value for TiO₂-based flexible devices. The bonded F atoms on the surface of TiO₂ promote the formation of Pb—F bonds and hydrogen bonds between F⁻ and FA/MA organic cations, reinforcing interface binding of perovskite layer with TiO₂ ETL. This contributes to effective passivation of the surface trap states of perovskite film, resulting in enhancements of device efficiency and stability especially under UV light.

1. Introduction

During the past decade, tremendous attention has been paid to organic-inorganic hybrid perovskite solar cells (PSCs) owing to the peculiar properties of organometal halide perovskite light-absorbing materials, including tunable bandgaps, large absorption coefficients, high carrier mobilities, large carrier diffusion lengths, and small exciton binding energies.[1] Thanks to the continuous efforts on engineering not only the composition, phase, and morphology of the perovskite absorber layer but also the perovskite/electrode interfaces, the record power conversion efficiency (PCE) of PSCs has reached 25.5%.[2,3] Even so, several critical issues such as device stability,[4] scalability,[5] and flexibility[6] still hinder the commercialization road of PSCs.

Regular-structure (n–i–p) planar heterojunction (PHJ) are the most commonly used architectures for high-efficiency PSCs, in which an electron transport layer (ETL) sandwiched between the bottom transparent electrode and the perovskite layer...
atop plays an important role in efficient interfacial electron transport.[7] Various metal oxides such as TiO₂, SnO₂, ZnO, and Nb₂O₅ have been used as ETLs in the PHJ-PSCs, demonstrating different performances due to their difference on the electronic structures.[8] Among them, low-temperature (generally ≤150 °C) solution-processed TiO₂ nanocrystals are compatible with low-cost fabrication and flexible devices, thus have been extensively applied.[9–11] Nonetheless, the inherent drawbacks of low-temperature solution-processed TiO₂ (LT-TiO₂), such as low electron mobility, high density of electronic trap states, and high photocatalytic activity, result in undesirable charge recombination at the ETL/perovskite interface and notorious instability of PSCs under ultraviolet (UV) light.[12,13] Such drawbacks of LT-TiO₂ can be overcome by either modulating its intrinsic electronic and band structures through elemental doping[14] or tailoring its electric properties and morphology via surface modifications.[15] In particular, despite of the success of elemental doping in modulating the intrinsic electronic and band structures of TiO₂,[16,15] up to now doping LT-TiO₂ by nonmetallic elements for applications as ETL of PSCs has been scarcely reported.[9] In 2016, Tan et al. developed a contact-passivation strategy by capping LT-TiO₂ nanoparticles with chlorine (Cl), and found that Cl-doping enhanced the contact of perovskite with TiO₂ and suppressed interfacial recombination, leading to improved device stability along with an improved PCE of 20.9%.[9] This limited report demonstrates that nonmetallic element doping of TiO₂ is quite effective in not only modulating the intrinsic electronic and band structures of TiO₂ itself but also promoting the quality of the perovskite layer atop. Nevertheless, it is unknown whether Cl-doping can tackle the high photocatalytic activity drawback of TiO₂ or not, thus the instability issue of TiO₂-based PSC devices under UV light remains unsolved. Hence, exploiting novel nonmetallic elements to dope LT-TiO₂ for not only improved ETL performance but also inhibited photocatalytic activity is highly desirable.

Herein, we develop a simple one-step nonhydrolytic method to in situ surface fluorinate LT-TiO₂ nanocrystals, affording formation of Ti-F bonds and consequently increased electron mobility, decreased density of electronic trap states, and inhibited photocatalytic activity of TiO₂ due to preferentially binding of fluorine (F) atom onto the (001) facet of anatase TiO₂. Fluorinated TiO₂ nanocrystals (abbreviated as F-TiO₂) is applied as a novel ETL in regular-structure K₀.₀₂Cš₀.₀₁Fₐ₀.₈M₀a₀.₁₂Pₐ₁₂.₅₅Bₐ₀.₄₅ (abbreviated as KCsFAMA) PHJ-PSC devices, delivering a champion PCE of 22.68%, which is among the highest PCEs for PHJ-PSCs based on LT-TiO₂ ETLs. F-doping not only reinforces interface binding of KCsFAMA perovskite layer with TiO₂ ETL, but also contributes to effective passivation of the surface trap states of perovskite film as deduced from a series of characterizations and theoretical calculations. As a result, dramatic enhancements of device efficiency and stability especially under UV light are achieved.

2. Results and Discussion

Fluorine (F) has the highest electronegativity among all elements, and it has been reported that incorporation of F⁻ anion in perovskite layer led to passivation of both anion and cation vacancies of perovskite and consequently improved PSC device efficiency along with enhanced thermal and environmental stability.[16] Besides, it has been reported that the photocatalytic activity of TiO₂ may be inhibited by surface fluorine termination.[17,18] Hence, we manage to employ F as a dual-functional dopant of TiO₂ so as to investigate the feasibility of improving PSC efficiency and enhancing UV-light stability in our present study.

In situ surface fluorination of TiO₂ nanocrystals was fulfilled by a one-step nonhydrolytic sol–gel method.[11] Briefly, TiF₄ was doped into a TiCl₄ precursor solution dissolved in anhydrous ethanol with variable F:Ti molar ratios of 4%, 8%, 12%, 20%, and 50% (nominal abbreviated as 4%-F-TiO₂, 8%-F-TiO₂, 12%-F-TiO₂, 20%-F-TiO₂, and 50%-F-TiO₂, respectively). F-doped TiO₂ (F-TiO₂) colloidal nanocrystals were obtained by dispersing the alcoholized TiCl₄ in anhydrous benzyl alcohol in ethanol with titanium(diisopropoxide) bis(2,4-pentanediolate) (TIPD) as the stabilizer (see the Experimental Section for details). Because of the much larger electronegativity of F than Cl, we found that TiF₄ with stronger Ti-F ionic bonds is much more stable than TiCl₄ during the alcoholysis process, thus Cl was completely removed by ligand exchange of TIPD and only F was doped in the final TiO₂ colloidal nanocrystals. The optimized F:Ti molar ratio is determined to be 12% according to the device performance discussed below. To simplify the analyses, hereafter all characterizations are based on typical F:Ti molar ratios of 4% (low), 12% (optimal), and 50% (excess) unless otherwise stated. According to a comparison of the transmission electron microscopy (TEM) images of F-TiO₂ and the pristine TiO₂ nanocrystals (Figure S1, Supporting Information), the obtained TiO₂ nanocrystals are quasi-monodispersed, and F-doping leads to increase of the average particle size. This is confirmed by analyzing their corresponding high-resolution (HR) TEM images (Figure 1a–c), revealing that the lateral size of TiO₂ nanocrystals increases from 3.95 nm (pristine TiO₂) to 4.97 and 8.43 nm for 12%-F-TiO₂ and 50%-F-TiO₂, respectively. The lattice fringes of (101) plane with space distance of ≈3.5 Å are clearly observed for all samples, while those of (002) planes with space distance of 4.7 Å observed for the pristine TiO₂ and 12%-F-TiO₂, disappear for 50%-F-TiO₂, which shows clearly lattice fringes of (004) plane instead. This indicates that F doping induces change of the exposed plane of TiO₂ surface.

The effect of F-doping on the crystalline phase of TiO₂ is investigated by powder X-ray diffraction (XRD). As shown in Figure 1d, the diffraction patterns of F-TiO₂ and the pristine TiO₂ nanocrystals, are in agreement with the standard pattern of crystalline anatase TiO₂ (JCPS:21-1272). Interestingly, the full width at half-maximum (FWHM) of the diffraction peaks (101) and (200) of F-TiO₂ decrease, while that of the diffraction peak (004) of F-TiO₂ increases relative to those of the pristine TiO₂. This indicates that F-doping leads to preferential growth of TiO₂ crystal along (100) facet with the increase of the crystal size (200) facet estimated by Scherrer’s equation (see Table S1 in the Supporting Information). Such a crystal shape change of TiO₂ may be caused by the preferential binding of F atoms onto the (001) facets of anatase TiO₂, resulting in reduced surface energy and kinetically inhibiting the crystal growth in the direction perpendicular to (001) facets, and consequently (001) facets are preferentially exposed.[18,19] Since the photocatalytic activity of TiO₂ is sensitively dependent on the exposed crystalline facet and surface fluorine termination, F-doping induced exposure of (001) facets is expected to weaken the photocatalytic activity of TiO₂.[17,18]
An intriguing question is whether F\(^{-}\) anion involved in TiF\(_4\) starting material exists as a dopant in the final TiO\(_2\) films. We carried out X-ray photoelectron spectroscopic (XPS) characterizations to probe the change of chemical composition of TiO\(_2\) films before and after fluorination. As shown in the XPS survey spectra (Figure S2, Supporting Information), no F 1s signal is detected for the pristine TiO\(_2\) film, whereas F 1s signal appears obviously for 12%-F-TiO\(_2\) film, confirming the existence of F in the final TiO\(_2\) films. The valence state of F within F-TiO\(_2\) is further studied by high-resolution F 1s XPS spectroscopy, indicating a symmetrical peak centered at 684.3 eV (Figure 1e). This corresponds to F\(^{-}\) anion that binds onto the surface of TiO\(_2\) via Ti—F ionic bonds.\(^{[18,20]}\) The actual atomic ratio of F:Ti is estimated to be 0.050 (see Table S2 in the Supporting Information). No any Cl signal is detected in both 12%-F-TiO\(_2\) and pristine TiO\(_2\) films, revealing no Cl contamination. Meanwhile, according to the Ti 2p XPS spectrum of 12%-F-TiO\(_2\), the Ti 2p\(_{1/2}\) and Ti 2p\(_{3/2}\) peaks with the binding energies of 464.5 and 458.7 eV shift positively by 0.1 eV relative to those of the pristine TiO\(_2\) (Figure 1f), agreeing with the formation of Ti—F ionic bonds due to the higher electronegativity of F than oxygen.\(^{[21]}\)

It is known that oxygen vacancies as the major defects exist in LT-TiO\(_2\) nanocrystals.\(^{[22,23]}\) We investigated the influence of F-doping on the oxygen vacancies by comparing the O 1s XPS spectra of the pristine TiO\(_2\) and 12%-F-TiO\(_2\) powders. As shown in Figure 1g, both the pristine TiO\(_2\) and 12%-F-TiO\(_2\) exhibit two asymmetric broad peaks, which can be deconvoluted into three peaks centered at \(\approx 530.2, 531.1, \) and 531.9 eV, attributed to the O\(^{2-}\) anion bonded with the Ti\(^{4+}\) cation in the stoichiometric TiO\(_2\) structure (O\(_{\text{M}}\)), the oxygen vacancies (O\(_{\text{V}}\)), and the hydroxyl groups bonding to TiO\(_2\) (OOH), respectively.\(^{[11]}\) Interestingly, after fluorination, the relative content of oxygen vacancies (O\(_{\text{V}}\)) within TiO\(_2\), which is estimated from the relative area of the O\(_{\text{V}}\) signal [O\(_{\text{V}}\)/(O\(_{\text{M}}\) + O\(_{\text{V}}\) + OOH)], decreases from 15.6% to 12.3% (Table S3, Supporting Information). This indicates that F-doping leads to passivation of the oxygen vacancies of TiO\(_2\).\(^{[24]}\) To understand the mechanism of F\(^{-}\) induced oxygen defect passivation of TiO\(_2\), we carry out density functional theory (DFT) calculations (see Note S4 in the Supporting Information for details). According to a comparison of the density of states (DOS) of the defective TiO\(_2\) before and after F incorporation, when only one F atom is doped within TiO\(_2\) unit, the incorporated F atoms tend to occupy the oxygen vacancies of TiO\(_2\), but have little influence on the defect energy level of the defective TiO\(_2\) (Figure S3e,f, Supporting Information). Surprisingly, with the increase of the number of doped F atoms from one to two, F may bond with the uncoordinated Ti in addition to occupying the oxygen vacancy, vanishing the defect energy level of TiO\(_2\) (Figure S3g,h, Supporting Information). However, upon increasing the number of doped F atoms to three, a new defect level appears near the valence band edge (Figure S3i,j, Supporting Information). The formation of Ti—F bonds on the surface of TiO\(_2\) may passivate oxygen vacancies and/or Ti dangling bonds on the surface of TiO\(_2\), thus efficiently suppressing electron–hole recombination. This is expected to enhance the...
electron mobility and decrease the photocatalytic activity of TiO$_2$ as discussed below.$^{[19,24-26]}$

Since the chemical composition and crystalline lattice structure determine the optical and electronic properties of TiO$_2$, it is necessary to probe the influence of F-doping on the optical and electronic properties of TiO$_2$. The optical transmission spectra of the pristine TiO$_2$ and F-TiO$_2$ films are compared in Figure S4 in the Supporting Information, revealing that F-TiO$_2$ films have higher optical transmittance in the range of 400–700 nm than the pristine TiO$_2$ film likely due to Fresnel interference.$^{[28]}$ Such an increase of in the optical transmittance allows more light to pass through the TiO$_2$ ETL entering perovskite layer, beneficial for light absorbance of perovskite layer.$^{[5]}$ On the other hand, F-doping imposes negligible influence on the UV–vis optical absorption of TiO$_2$, while the optical bandgap of TiO$_2$ estimated from the diffuse reflectance spectra increases slightly from 3.13 eV (the pristine TiO$_2$) to 3.17 eV (50% F-TiO$_2$) after F-doping (Figure S5, Supporting Information), consistent with the passivated surface oxygen vacancies after F doping.$^{[12]}$

The electron mobility of TiO$_2$ film is measured by the space charge limited current (SCLC) method with a sandwiched structure of indium tin oxide (ITO)/Ag/TiO$_2$/Ag.$^{[13]}$ The corresponding I–V curves for the electron-only devices based on different TiO$_2$ films are illustrated in Figure 1h, from which the electron mobility ($\mu_e$) of the pristine TiO$_2$, 4% F-TiO$_2$, 12% F-TiO$_2$, and 50% F-TiO$_2$ films are calculated to be $0.77 \times 10^{-4}$, $1.21 \times 10^{-4}$, $1.92 \times 10^{-4}$, and $5.29 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively (see Figure S6 and Table S4 in the Supporting Information). Clearly, the electron mobility increases dramatically by more than one order of magnitude for 50% F-TiO$_2$. This is interpreted by oxygen defect passivation and change of exposed crystalline plane after F doping.$^{[26,29]}$

To unravel the influence of F-doping on the photocatalytic activity of TiO$_2$, we evaluated the degradation rate of Rhodamine B (RhB) dye in the presence of TiO$_2$ nanocrystals photocatalysts under irradiation of a solar simulator. Figure 1i compares the photocatalytic activities of the pristine TiO$_2$, 4% F-TiO$_2$, 12% F-TiO$_2$, and 50% F-TiO$_2$ films, indicating that the photocatalytic activity of TiO$_2$ decreases obviously after F-doping, and the inhibition degree increases with the increase of the molar ratio of the incorporated F. However, after calcination at 600 °C in air for 3 h, the photocatalytic activity of 50% F-TiO$_2$ to degrade RhB was obviously higher than that of the pristine TiO$_2$ (Figure S7, Supporting Information). It has been reported that the photocatalytic activity of TiO$_2$ is primarily determined by the oxygen vacancy and Ti unsaturated site.$^{[17]}$ Hence, the inhibited photocatalytic activity of TiO$_2$ after F-doping is understandable since F-doping leads to passivation of the oxygen vacancy and Ti dangling bonds as discussed above.

We next employed scanning electron microscopy (SEM) and atomic force microscopy (AFM) to probe the influence of F-doping on the morphology of TiO$_2$ film, which is essential for the deposition of perovskite layer atop. Figure S8a–d in the Supporting Information compare the SEM images of the pristine TiO$_2$ and F-TiO$_2$ films deposited on ITO substrate, indicating that their overall film morphologies are similar. According to AFM measurements, the film smoothness of 12% F-TiO$_2$ is also comparable to that of the pristine TiO$_2$, as evidenced from their comparable root-mean-square (RMS) roughness, while increasing further the F content for 50% F-TiO$_2$ results in obvious increase of RMS roughness from 4.6 to 11.0 nm (Figure S8e–h, Supporting Information). Indeed, 50% F-TiO$_2$ film looks less uniform than the pristine TiO$_2$ and 12% F-TiO$_2$, composed of random aggregations and many pinholes. Such a rough and nonuniform film is likely due to the increase of lateral size of TiO$_2$ nanocrystals and expected to deteriorate the interfacial contact between TiO$_2$ ETL and perovskite, consequently detrimental for interfacial electron transport as discussed below.$^{[30]}$

It is then necessary to examine whether such morphological changes of TiO$_2$ film induced by F-doping affect the KCsFAMA perovskite films atop. We deposited KCsFAMA perovskite films under identical conditions onto different TiO$_2$ substrates, and examined the morphology and crystallinity of the perovskite film by using AFM, SEM, and synchrotron-based grazing incidence X-ray diffraction (GIXRD). As illustrated from the SEM images of the perovskite films deposited on different TiO$_2$ substrates (Figure 2a–d), all perovskite films appear uniform and dense without discernible pinholes, while an obvious increase of the average crystalline grain size from $\approx 390$ nm (the pristine TiO$_2$) to $\approx 410$ nm (4% F-TiO$_2$) and $\approx 470$ nm (12% F-TiO$_2$) is observed. Intriguingly, upon increasing further the F content for 50% F-TiO$_2$, the average grain size decreases to $\approx 460$ nm (Figure S9, Supporting Information). This reveals that F-doping may affect the crystal nucleation and crystallization kinetics of perovskite.$^{[16]}$ In addition, compared with the perovskite film deposited on the pristine TiO$_2$ substrate, the perovskites films deposited on F-TiO$_2$ substrates become smoother as deduced from their smaller RMS roughnesses (Figure S10, Supporting Information).

Figure 2e–h compares the 2D-GIXRD profiles of the KCsFAMA perovskite films deposited on different TiO$_2$ substrates obtained under an X-ray incident angle of 0.2°. The diffraction profiles of all perovskite films are similar, exhibiting several characteristic scattered rings at $q \approx 10$, 20, and 22.2 nm$^{-1}$ corresponding respectively to the (001), (002), and (012) crystal planes of perovskite. This feature is consistent with those reported in the literature.$^{[31]}$ After F-doping, all of the scattered rings of perovskite films look brighter than those of perovskite deposited on the pristine TiO$_2$, indicating that F-doping of TiO$_2$ leads to improved crystallinity of perovskite film atop. This statement is verified more intuitively by comparing the radially integrated intensity of the rings at $q$ between 5 and 30 nm$^{-1}$ (Figure S11a, Supporting Information). Clearly, the (001), (002), and (012) peak intensities increase for the perovskite films deposited on the F-TiO$_2$ substrates relative to those for the perovskite on the pristine TiO$_2$. Besides, crystalline orientation of perovskite films deposited on different TiO$_2$ substrates are compared in the azimuthal scan profiles along the ring of (001) plane extracted from the 2D-GIXRD patterns (Figure S11b, Supporting Information). Unlike the perovskite film on the pristine TiO$_2$ substrate which shows the lowest intensity at 90°, the peaks at 90° for the perovskite films on F-TiO$_2$ substrates become the most intense, suggesting that F-doping of TiO$_2$ affords preferential out-of-plane orientation of (001) plane for perovskite film (Figure 2j).$^{[31]}$ This conclusion is solidified by comparing the cross-sectional SEM images of the perovskite films deposited on different TiO$_2$ substrates, revealing that the crystal grains of perovskite film ($\approx 425$ nm thick) deposited on
12%-F-TiO2 (≈50 nm thick) are columnar with vertical orientations, whereas the control perovskite film deposited on the pristine TiO2 exhibits random orientation of crystalline grains (Figure 2k,l). Such oriented growth of perovskite crystal grain is expected to promote the vertical charge transport within the perovskite layer.[31,32]

To understand the origin of F-induced oriented growth of perovskite crystal grains, we carried out a series of characterizations to probe the interaction of F-TiO2 with KCsFAMA perovskite. We first spin-coated a 50%-F-TiO2 nanocrystals suspension dispersed in isopropanol onto KCsFAMA perovskite film, and used XPS to study the interactions of F-TiO2 with KCsFAMA perovskite film. As shown in the high-resolution Pb 4f XPS spectra, for the perovskite/F-TiO2 film the Pb 4f5/2 and Pb 4f7/2 signals detected at 142.9 and 138.0 eV both shift positively by 0.1 eV relative to those detected for the pristine TiO2 (Figure S12a, Supporting Information), suggesting the formation of Pb–F ionic bonds at perovskite/F-TiO2 interface.[33] The Pb–F bond is expected to suppress Pb–I antisite defects at the perovskite/TiO2 interface, as discussed further below.[9] Besides, N 1s XPS signal also shifts positively for the perovskite/F-TiO2 film (Figure S12b, Supporting Information). Given the strong electronegativity of fluorine, such a shift of N 1s peak suggests the change of N=H bonding within MA/FA cations, which is resulted from the formation of hydrogen bonds (N=H···F) between fluorine and MA/FA cations.[16] To verify this, we carried out solid-state 19F NMR measurements of a mixture of 50%-F-TiO2, and formamidinium iodide (FAI), and find that the 19F signal of the original 50%-F-TiO2 shifts toward downfield after mixed with FAI (Figure S12c, Supporting Information), confirming the formation of N–H···F hydrogen bonds between fluorine and MA/FA cations.[14] As a result, the doped F atom bridges TiO2 and perovskite via the Pb–F ionic bonds and N–H···F hydrogen bonds are expected to reinforce the interface binding of perovskite layer with TiO2, benefiting the oriented growth of perovskite crystal grains (Figure S12d,e, Supporting Information).[16]

Given that F-doping not only leads to passivation of the oxygen vacancy and increase of electron mobility of TiO2, but also induces oriented growth of KCsFAMA perovskite crystal grains, it is necessary to investigate whether such effects benefit PSC device performance or not. We incorporated F-TiO2 nanocrystals as novel ETLs and fabricated the regular-structure (n–i–p) PHJ-PSC devices with the structure of ITO/F-TiO2/KCsFAMA perovskite/2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (spiro-OMeTAD)/Au (Figure 3a). Figure 3b compares the current density–voltage (J–V) curves of the champion devices based on different TiO2 ETLs measured under irradiation of 100 mW cm−2 (AM1.5G). The corresponding photovoltaic parameters, including open-circuit voltage (Voc), short-circuit current (Jsc), fill factor (FF), PCE, series resistance (Rs), and shunt resistance (Rsh), obtained on the basis of the statistical data of over 60 devices fabricated independently are summarized in Table 1 (see also Figure S13 and Table S5 in the Supporting Information for the photovoltaic data obtained from F-TiO2 ETLs with other F:Ti molar ratios). The control device based on the pristine TiO2 ETL exhibits a best PCE of
Figure 3. a) Schematic structure of ITO/F-TiO2/KCsFAMA perovskite/spiro-OMeTAD/Au device. b) J–V curves of the champion devices based on different TiO2 ETLs. The scanning direction is from open-circuit voltage to short circuit (reverse) with a scan rate of 0.1 V s⁻¹. c) The stabilized photocurrent and power output of the PSC devices based on 12%-F-TiO2 ETL measured at the maximum power points (1.05 V). d) J–V curves of the devices based on pristine TiO2 and 12%-F-TiO2 ETLs under reverse and forward scans with a scan rate of 0.1 V s⁻¹. e) EQE spectra of the devices based on pristine TiO2 and 12%-F-TiO2 ETLs. f) J–V curves of the champion flexible devices based on pristine TiO2 and 12%-F-TiO2 ETLs. The scanning direction is from open-circuit voltage to short circuit (reverse) with a scan rate of 0.1 V s⁻¹. The inset shows the photograph of a flexible device.

Table 1. Photovoltaic parameters of the perovskite solar cells deposited on different TiO2 ETLs under one sun illumination (AM 1.5G, 100 mA cm⁻²).

| ETL          | Molar ratio of F:Ti [%] | \(V_{oc}[V]\) | \(J_{sc}[mA cm^{-2}]\) | FF[%] | PCE[%] | \(R_s[\Omega cm^2]\) | \(R_{sh}[\Omega cm^2]\) |
|--------------|------------------------|----------------|--------------------------|-------|--------|------------------------|------------------------|
| Pristine TiO2| 0                      | 1.16 ± 0.02    | 22.35 ± 0.79             | 73.86 ± 2.82 | 19.17 ± 1.11 | 4.58                  | 2272.36               |
|              | Champion               | 1.17           | 23.23                    | 77.33  | 21.09  | 3.79                   | 3578.55               |
| 4%-F-TiO2    | 4                      | 1.16 ± 0.02    | 22.74 ± 0.74             | 75.11 ± 2.20 | 19.87 ± 1.05 | 4.28                  | 2919.47               |
|              | Champion               | 1.18           | 23.47                    | 78.69  | 21.80  | 3.25                   | 3433.31               |
| 12%-F-TiO2   | 12                     | 1.17 ± 0.02    | 22.90 ± 0.61             | 77.03 ± 1.90 | 20.66 ± 0.97 | 3.89                  | 3706.49               |
|              | Champion               | 1.21           | 23.36                    | 80.25  | 22.68  | 3.32                   | 8534.90               |
| 50%-F-TiO2   | 50                     | 1.15 ± 0.03    | 22.96 ± 0.68             | 74.89 ± 2.38 | 19.79 ± 0.97 | 4.08                  | 2740.63               |
|              | Champion               | 1.16           | 23.71                    | 78.05  | 21.55  | 3.95                   | 9206.34               |

The molar ratio for F⁻ relative to Ti⁴⁺ in the raw solution. \(R_s\) and \(R_{sh}\) are given by the PCE measurement system. Averaged over 60 devices fabricated independently.

21.09% calculated from a \(V_{oc}\) of 1.17 V, a \(J_{sc}\) of 23.23 mA cm⁻², and an FF of 77.33%. Upon using F-TiO₂ ETL, both the average and best PCEs increase obviously, and the device based on 12%-F-TiO₂ ETL delivers the highest champion PCE of 22.68%, derived from a \(V_{oc}\) of 1.21 V, a \(J_{sc}\) of 23.36 mA cm⁻², and an FF of 80.25%. Thus, the optimized F:Ti molar ratio is determined to be 12%. Besides, the stabilized photocurrent and steady PCE for the champion 12%-F-TiO₂ device loaded at the maximum power point (\(V_{mpp}\) ≈ 1.05 V) over 200 s reach 21.55 mA cm⁻² and 22.63%, respectively, significantly higher than those of the control device (Figure 3c; Figure S14, Supporting Information). Moreover, both 12%-F-TiO₂ and pristine TiO₂ devices exhibit negligible hysteresis, while the hysteresis index defined as \([\text{PCE(forward)}/\text{PCE(reverse)}]-1\) slightly decreases for 12%-F-TiO₂ device (Figure 3d; Table S6, Supporting Information). Remarkably, to our knowledge the record PCE for the PHJ-PSC devices based on low-temperature solution-processed TiO₂ ETLs reported up to now is 22.7%, hence the highest PCE of 22.68% obtained in our present work is among the highest PCEs for devices based on LT-TiO₂ ETLs (see Table S7 and Figure S15 in the Supporting Information).

We next compared the three key photovoltaic parameters (\(V_{oc}\), \(J_{sc}\), and FF) of 12%-F-TiO₂ and pristine TiO₂ devices based on the statistic data of over 60 independent devices, and find that \(V_{oc}\), \(J_{sc}\), and FF all increase for 12%-F-TiO₂ device, while the PCE enhancement from 19.17% to 20.66% (~7.8% enhancement) is primarily resulted from increases of both \(J_{sc}\) (from 22.35 to 22.90 mA cm⁻², ~2.5% enhancement) and FF (from 73.86% to 77.03%, ~4.3% enhancement) (see Table 1 and Figure S16 in the Supporting Information). The increase of \(J_{sc}\) is corroborated by external quantum efficiency (EQE) measurements, indicating that the overall EQE responses of 12%-F-TiO₂ devices are slightly higher than that of the control pristine TiO₂ device (Figure 3e), consequently a larger integrated \(J_{sc}\) is obtained. The superior ETL performance of F-TiO₂ along with its low-temperature solution-processibility stimulates us to evaluate its suitability for flexible PSC devices. Similar to rigid ITO-based devices, flexible PSCs based on polyethylene naphthalate (PEN)
substrates were fabricated using the same process. The $J-V$ curves of the champion PEN/ITO/F-TiO$_2$/KCsFAMA perovskite/spiro-OMeTAD/Au flexible PSC devices based on the pristine TiO$_2$ and F-TiO$_2$ ETLs measured under irradiation of 100 mW cm$^{-2}$ (AM 1.5G) are compared in Figure 3f, and the corresponding statistical photovoltaic parameters of over 20 devices are summarized in Table S8 in the Supporting Information. Similar to the case of ITO-based devices, all flexible PSC devices based on F-TiO$_2$ ETLs show higher average and champion PCEs, and 12% - F-TiO$_2$ devices deliver the highest values. This result reveals that F-doping strategy is universal for both rigid and flexible substrates. In particular, the highest PCE of 18.26% obtained for 12% - F-TiO$_2$ flexible PSC device appears to the record value for flexible PHJ-PSC based on LT-TiO$_2$ ETLs (Table S9 and Figure S17 in the Supporting Information).

To understand the change of the $V_{oc}$ value after F-doping, the energy level alignment between the TiO$_2$ ETL and perovskite needs to be checked. We used ultraviolet photoelectron spectroscopy (UPS) to probe the effect of F-doping on the work function of TiO$_2$. The determined work function ($W_F$) of the pristine TiO$_2$, 4% - F-TiO$_2$, 12% - F-TiO$_2$, and 50% - F-TiO$_2$ are 4.10, 4.15, 4.26, and 4.31 eV, respectively (see Figure S18 in the Supporting Information), revealing that F-doping leads to the increase of the work function of TiO$_2$. Such a downshift of the Fermi level of TiO$_2$ would result in the decrease of built-in potential ($V_B$) in the device, consequently leading to the decrease of $V_{oc}$ for 50% - F-TiO$_2$ device.$^{[37]}$

It is known that the existence of defects of the perovskite, which mainly distribute on the surface of polycrystalline film, is an intrinsic factor deteriorating the device performance.$^{[38]}$ We investigated the effect of F-doping on defect passivation of perovskite film by measuring the electron trap-state density using SCLC method based on an electron-only device with a structure of ITO/F-TiO$_2$/KCsFAMA perovskite/spiro-OMeTAD/Ag.$^{[39]}$ According to a comparison of the $I-V$ curves of the devices based on different TiO$_2$ ETLs (Figure S19, Supporting Information), the electron trap-state density ($n_t$) within the KCsFAMA perovskite films deposited on 4% - F-TiO$_2$, 12% - F-TiO$_2$, 50% - F-TiO$_2$, and the pristine TiO$_2$ substrates are calculated to be 5.90 $\times$ 10$^{15}$, 3.59 $\times$ 10$^{15}$, 9.49 $\times$ 10$^{15}$, and 6.67 $\times$ 10$^{15}$ cm$^{-3}$, respectively (see Table S10 in the Supporting Information for detailed analyses). Hence, 12% - F-TiO$_2$ device exhibits the lowest electron trap-state density, which is decreased by around 46% relative to that for the control device. This is understandable since it has been reported that introduction of a moderate amount of F suppressed the FA vacancies defect at the surface of KCsFAMA perovskite through forming hydrogen bonds (N–H···F)$^{[16]}$. However, excess F-doping in the case of 50% - F-TiO$_2$ results in increase of the electron trap-state density from 6.67 $\times$ 10$^{15}$ to 9.49 $\times$ 10$^{15}$ cm$^{-3}$. To gain deeper insight into the mechanism of F-induced defect passivation of perovskite, we quantitatively measured the deep traps of perovskite by the deep-level transientspectroscopy (DLTS).

Figure 4a compares the DLTS spectra of the devices based on different TiO$_2$ ETLs.$^{[40]}$ The activation energy ($E_{T} - E_{V}$ or $E_{C} - E_{T}$) and the concentration ($N_{T}$) of traps can be obtained from Arrhenius plots and the fitting results (see Figure S20 and Table S11 in Note S23 in the Supporting Information for details). Two negative peaks are observed for all devices, which are assigned to hole traps (H) in n-type perovskite films, labelled as D$_1$ and D$_2$, respectively.$^{[41]}$ According to the activation energy of the deep traps, D$_1$ and D$_2$ could be attributed to antisite defects (such as I$_{p}$ or F$_{p}$) and Pb$_p$.$^{[42]}$ After F doping, the D$_1$ peaks shift to higher temperatures, suggesting

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Figure 4. a) DLTS spectra of the devices based on different TiO$_2$ ETLs. b) Steady-state PL and c) TRPL spectra of perovskite films deposited on different TiO$_2$ substrates. Responses of d) $J_{sc}$ and e) $V_{oc}$ on the irradiation intensity of the devices based on different TiO$_2$ ETLs. f) Nyquist plots of the devices based on different TiO$_2$ ETLs measured in the dark under a reverse potential of 1.0 V. The fitted curves are shown as solid lines, and the experimental data are shown as corresponding points. Inset: The equivalent circuit model employed for the fitting of the impedance spectra.
the higher activation energies of the F$_{\text{Pb}}$ defect than that of I$_{\text{Pb}}$ defects (see Note S24 in the Supporting Information for details). The trap-state densities of D$_{\text{1}}$ defect within perovskite films based on different TiO$_2$ ETLs decrease from 9.72 × 10$^{14}$ (the pristine TiO$_2$) to 6.69 × 10$^{14}$ (4%-F-TiO$_2$), 4.75 × 10$^{14}$ (12%-F-TiO$_2$), and 3.82 × 10$^{14}$ (50%-F-TiO$_2$) (see Figure S20 and Table S11 in Note S23 in the Supporting Information for details). The decreased D$_{\text{1}}$ trap-state density is resulted from the higher formation energy of F$_{\text{Pb}}$ defect (3.022 eV) than that of I$_{\text{Pb}}$ defect (2.869 eV) as predicted by DFT calculations (see Table S12 in the Supporting Information for details). In addition, the trap-state densities of D$_{\text{2}}$ defect associated with Pb$_n$ are calculated to be 4.01 × 10$^{14}$, 2.20 × 10$^{14}$, 6.30 × 10$^{14}$, and 5.71 × 10$^{14}$ cm$^{-2}$ within the perovskite films deposited on 4%-F-TiO$_2$, 12%-F-TiO$_2$, 50%-F-TiO$_2$, and the pristine TiO$_2$ substrates, respectively. Hence, partial substitution of F$^-$ on the surface of perovskite by F$^-$ can effectively suppress the Pb$_n$ antisite defect. On the contrary, the 50%-F-TiO$_2$ device exhibits the increased concentrations of D$_{\text{2}}$ defects peaks relative to the 12%-F-TiO$_2$ device, indicating that excess F doping leads to increased Pb$_n$ antisite defects. It is known that deep-level defects are the predominant traps sources for nonradiative recombination losses, resulting in deficit of $V_{\text{oc}}$.[43] Therefore, the suppressed deep-level antisite defects after F-doping explains the slight increase in $V_{\text{oc}}$ value.

In order to unveil the factors responsible for the increases of $J_{\text{sc}}$ and FF, we implemented a series of characterizations to elucidate the influence of F-doping on the charge carrier dynamics of the device. It has been reported that the interfacial charge extraction sensitively determines $J_{\text{sc}}$.[44] The electron extraction and electron–hole recombination dynamics at the TiO$_2$/perovskite interface is first investigated by steady-state and time-resolved photoluminescence (TRPL) spectroscopies. Figure 4b compares the steady-state PL spectra of the KCsFAMA perovskite films deposited on different TiO$_2$ substrates measured under an excitation wavelength of 460 nm, indicating that the characteristic PL peak at 756 nm of KCsFAMA perovskite film deposited on the pristine TiO$_2$ substrate is quenched for those on 12%-F-TiO$_2$ and 50%-F-TiO$_2$, whereas such a PL intensity increases for the case of 4%-F-TiO$_2$. Since the PL intensity of perovskite film is a balance of charge transfer and nonradiative recombination at interfaces,[45] the increase of PL intensity for 4%-F-TiO$_2$ may result from the suppression of nonradiative recombination by the passivation of perovskite defects.[44] Upon increasing the F-doping ratio, the quenching of PL peak for 12%-F-TiO$_2$ and 50%-F-TiO$_2$ is resulted from the more dramatic increases of the electron mobility of TiO$_2$, as discussed above, leading to more efficient electron transfer from the KCsFAMA perovskite to TiO$_2$ ETL, consequently contributing to increase of $J_{\text{sc}}$. This conclusion is confirmed by the result of TRPL, revealing that the carrier lifetimes ($\tau$) of the KCsFAMA perovskite films deposited on 12%-F-TiO$_2$ and 50%-F-TiO$_2$ (246.87 and 219.51 ns, respectively) are smaller than that on the pristine TiO$_2$ (252.92 ns; Figure 4c; Table S13, Supporting Information).

We next investigate the dependence of $J_{\text{sc}}$ and $V_{\text{oc}}$ on light intensities ($I$) so as to understand further the recombination kinetics within the device.[40,47] The bimolecular recombination kinetics of the devices are probed by the ideality factors ($\alpha$) extracted from the equation $J_{\text{sc}} \propto I^\alpha$, and the corresponding fitting curves are plotted in Figure 4d. The $\alpha$ values of devices based on the pristine TiO$_2$, 4%-F-TiO$_2$, 12%-F-TiO$_2$, and 50%-F-TiO$_2$ are 0.85, 0.89, 0.91, and 0.88, respectively. The largest $\alpha$ value of the 12%-F-TiO$_2$ device, which is more close to unity, indicates the least bimolecular recombination.[40] Besides, the dependence of voltage to the light intensity is characterized so as to reveal the trap-assisted Shockley–Read–Hall (SRH) monomolecular recombination of device according to the equation $V_{\text{oc}} = nkT/\alpha e + \text{constant}$ (where $n$ is the ideality factor, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $e$ is the elementary charge).[47]

The dependence of $V_{\text{oc}}$ on the logarithm of the incident light intensity are shown in Figure 4e, from which the extracted $n$ values of devices based on the pristine TiO$_2$, 4%-F-TiO$_2$, 12%-F-TiO$_2$, and 50%-F-TiO$_2$ are determined to be 1.44, 1.25, 1.11, and 1.21, respectively. The $n$ value of the 12%-F-TiO$_2$ device is the closest to unity, suggesting the most effective suppression of the monomolecular SRH recombination. The largest suppression of both bimolecular and monomolecular SRH recombinations for the 12%-F-TiO$_2$ devices is due to the passivation of antisite defects of perovskite and increased electron mobility of TiO$_2$ as discussed above, which contribute directly to the increase in FF.[11,46]

The interfacial charge transport properties of the PSC devices based on different TiO$_2$ ETLs are probed by the electrochemical impedance spectroscopy (EIS) measured in the dark under a reverse potential of 1.0 V.[48] Figure 4f presents the Nyquist plots of devices based on different TiO$_2$ ETLs and the corresponding fitted curves obtained on the basis of a commonly used equivalent circuit model (see the inset in Figure 4f). The fitted parameters of $R_{\text{co}}$ (contact resistance) and $R_{\text{rec}}$ (recombination resistance) corresponding respectively to the electron transport and the electron–hole recombination are listed in Table S14 in the Supporting Information.[11] Compared to the control device, the $R_{\text{co}}$ values of F-TiO$_2$ devices decrease along with the increase of $R_{\text{rec}}$ values, revealing that F-doping enhances the electron transport and suppresses the electron–hole recombination at TiO$_2$/perovskite interface. In this sense, the smallest $R_{\text{co}}$ value and largest $R_{\text{rec}}$ value of 12%-F-TiO$_2$ device indicate the most efficient interfacial electron transport, contributing directly to the increase of $J_{\text{sc}}$.[13]

In the end, we examined the effect of F-doping on the ambient, UV-light, and thermal stability of the PSC devices by storing the devices under different conditions. First, the storage lifetime of the unencapsulated devices was monitored in ambient condition (temperature: 25 °C; relative humidity: 35%) for over 110 days. Compared to the control device based on the pristine TiO$_2$ ETL for which PCE drops to ≈80% of the initial value due to the decomposition of the KCsMAFA perovskite,[49] the 12%-F-TiO$_2$ device exhibits improved stability with PCE retaining 86% after 110 days (Figure 5a; Figure S22, Supporting Information). This indicates improved resistance to the attack of the moisture for 12%-F-TiO$_2$ device owing to the improved quality and passivated defects of the perovskite film as discussed above.[9,50] Besides, the UV-light stability of the devices encapsulated with ethylene was also evaluated under high-voltage mercury lamp irradiation (500 W) with a 365 nm cutoff filter (temperature: 30 °C; relative humidity: 80%). As shown in Figure 5b, the 12%-F-TiO$_2$ device retains 68% of the initial PCE after 26 h continuous UV light irradiation, whereas PCE of the control device degrades to nearly zero after only 10 h UV light irradiation. This reveals that F-doping significantly increase the UV-light stability of the device. Such an increase of UV-light stability should result from the inhibited
Photocatalytic activity of TiO₂ after F-doping as discussed above. Moreover, the thermal stability of the unencapsulated device was examined by aging them under continuous heating at 85 °C in a dark nitrogen atmosphere in a glove box. The PCE of the 12%-F-TiO₂ device decays very slowly and the PCE retains 83% of the initial value after 48 h, while the PCE of the control devices drops to ≈20% only (Figure 5c). This reveals that F-doping improves the thermal stability of devices as well.

3. Conclusion

In summary, LT-TiO₂ nanocrystals were in situ fluorinated via a simple one-step nonhydrolytic method, and the fluorinated TiO₂ nanocrystals (F-TiO₂) were applied as a novel ETL in regular-structure KCsFAMA P3HT-PSC devices, affording a champion PCE of 22.68%, which is among the highest PCEs for devices based on LT-TiO₂ ETLs. F-doping leads to formation of Ti–F bonds and consequently increased electron mobility, decreased density of electronic trap states and inhibited photocatalytic activity of TiO₂ due to preferentially binding of fluorine (F) atom onto the (001) facet of anatase TiO₂. Furthermore, F-doping not only reinforces interface binding of KCsFAMA perovskite layer with TiO₂ ETL through formation of Pb–F ionic bonds and N–H⋯F hydrogen bonds between F and MA/FA cations, but also contributes to effective passivation of the surface trap states of perovskite film. As a result, in addition to efficiency enhancement, F-doping leads to improvements of the ambient and thermal stabilities of PSC devices, especially UV-light stability due to inhibited photocatalytic activity of TiO₂. With these findings, our study paves the way for low-temperature fabrication of high-efficiency perovskite solar cells.

4. Experimental Section

Materials: The ITO glass substrate with a sheet resistance of 10 Ω sq⁻¹ was purchased from Shenzhen Nan Bo Group, China. All the chemicals were used as received, including FAI (Dyesol), methylammonium bromide (MABr, Dyesol), lead iodide (PbI₂, 99.999%, TCI), lead bromide (PbBr₂, 99.999%, Alfa Aesar), KI and CsI (MAI, Xi’an Polymer Light Technology Corp), TiCl₄ (GR, 99.5%, Aladdin), TiF₄ (Alfa Aesar), TIPD (TCI), spiro-OMeTAD (1 M company), and Li-bis(trifluoromethanesulfonyl)imide (Li-TFSI, Sigma). Dimethylformamide (DMF), benzyl alcohol, chloroform, and dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich. All materials were used as received without further purification.

Syntheses of F-TiO₂ Nanocrystals: The pristine TiO₂ nanocrystals were synthesized by using a modified nonhydrolytic sol–gel method with all procedures done in the ambient condition.[4,8] First, 0.5 mL TiCl₄ was injected drop by drop into 2 mL cold anhydrous ethanol with strong stirring. After the solution cooled down to room temperature, 10 mL of anhydrous benzyl alcohol was added to the previous solution and stirred for 10 min. The mixed solution was firmly sealed and stored without stirring in an oil bath pan at 85 °C for 12 h. The product of TiO₂ nanocrystals was then precipitated from the as-obtained solution by the addition of diethyl ether and isolated by centrifugation at 5000 rpm for 2 min. The solid was subsequently washed by adding anhydrous ethanol and diethyl ether, followed by a similar centrifugation step (5000 rpm for 2 min) for three times.

The F-TiO₂ nanocrystals were obtained with a similar approach except that TiF₄ was doped into a TiCl₄ solution dissolved in anhydrous ethanol as a precursor with variable F:Ti molar ratios of 4%, 8%, 12%, 20%, and 50% (nominally abbreviated as 4%-F-TiO₂, 8%-F-TiO₂, 12%-F-TiO₂, 20%-F-TiO₂, and 50%-F-TiO₂, respectively). To stabilize the as-obtained TiO₂ and F-TiO₂ nanocrystals, the washed nanocrystals were dispersed in anhydrous ethanol (concentration of around 5 mg mL⁻¹) by the addition of TIPD (15 µL mL⁻¹).

Device Fabrication: A patterned ITO glass substrate was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol. The as-prepared TiO₂ nanocrystals were spin-coated onto the ITO substrate at 5000 rpm for 40 s twice, and then these samples were annealed at 150 °C for 25 min in air under ambient pressure. The following coating steps were performed under argon atmosphere inside a glovebox. For the fabrication of KCsFAMA perovskite, the KCsFAMA precursor solution (1.3 m) was prepared with molar ratios of PbI₂/PbBr₂ = 3:1.02:1, FAI/MABr = 1.02 (a), KI/CsI/(FAI-MABr) = 0.025:0.05:0.95, PBI₂/FAI = 1.1:1, and PbBr₂/MABr = 1:0.2. The perovskite films were deposited onto the TiO₂ substrates with two-step spin coating procedures. The first step was 2000 rpm for 10 s with an acceleration of 200 rpm s⁻¹. The second step was 6000 rpm for 30 s with a ramp-up of 2000 rpm s⁻¹. Chlorobenzene (100 µL) was dropped on the spinning substrate during the second spin-coating step at 15 s before the end of the procedure. The substrate was then immediately transferred on a hotplate and heated at 100 °C for 60 min, followed by cooling down to room temperature naturally.

For the fabrication of KCsFAMA-based flexible perovskite solar cells, the processes and materials used were exactly the same as the rigid perovskite solar cells, except that the PEN/ITO (Pechell, Japan) instead of ITO glass was used as the substrate.

Measurements and Characterization: The current density–voltage (J–V) characterizations were measured by a Keithley 2400 source measurement unit under simulated AM 1.5 irradiation (100 mW cm⁻²) with a standard xenon-lamp-based solar simulator (Oriel Sol 3A, USA), which was calibrated with a monocrystalline silicon reference cell (Oriel P/N 91150 V, with KG-5 visible color filter) calibrated by the National Renewable Energy Laboratory (NREL). Around 60 devices were fabricated and measured independently under each experimental condition to confirm the reproducibility of the result and to obtain the statistical histograms of the
photovoltaic parameters. The EQE measurements were carried out on an ORIEL Intelligent Quantum Efficiency (IQE) 200TM Measurement system established with a tunable light source. To evaluate the UV-light stability of the devices, a high-voltage mercury lamp irradiation (500 W, China Education Au-light) with a 365 nm cutoff filter (QD 365 nm, China Education Au-light) was used.

SEM and EDS measurements were attained via a field-emission scanning electron microscope (FEI Apero). AFM images were carried out on a XE-7 scanning probe microscope in noncontact mode (Park systems, Korea). XPS measurements were performed on a Thermo ESCALAB 250 instrument with a monochromatized Al Kx X-ray source in vacuum. The XRD patterns were obtained on a Rigaku SmartLab X-ray diffractometer with Cu-K radiation (0.154 nm).

UV–vis spectroscopy was recorded on a UV–vis–NIR 3600 spectrometer (Shimadzu, Japan). The steady-state PL spectra were recorded by employing an Edinburgh Instruments FLS920 fluorescence spectrometer with an excitation wavelength of 460 nm. The TRPL spectra were measured via the time-correlated single-photon counting method with a Picoquant GmbH Solea Supercontinuum Laser. A picosecond pulsed diode laser at 543 nm with a pulse width of 104 ps was used as the excitation source.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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