Efficient and Stable Inverted Perovskite Solar Cells Incorporating Secondary Amines

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Low-cost and high-efficiency solar cells are attractive candidates to meet the growing demand for renewable energy. Silicon solar cells have reached a power conversion efficiency (PCE) of 26.6%,[1] approaching their theoretical limit; tandem solar cells generate a total power that exceeds what each subcell can generate individually. Perovskites represent a particularly attractive candidate for pairing with silicon, and silicon:perovskite tandem solar cells have demonstrated a total PCE of 28%.[7]

In a tandem solar cell, two cells stacked mechanically[2–4] or monolithically[5,6] generate a total power that exceeds what each subcell can generate individually. Perovskites represent a particularly attractive candidate for pairing with silicon, and silicon:perovskite tandem solar cells have demonstrated a total PCE of 28%.[7]

When constructing tandem solar cells, minimizing parasitic absorption in the window layers through which the light passes before reaching perovskite and silicon absorbers is crucial to reach high efficiency.[5] In the most efficient PSCs—which use a normal (n–i–p) architecture—hole transport layers (HTLs) with ionic dopants deposited on top of the perovskite act as a window layer.[8–10] These HTLs have parasitic absorption, and they also accelerate the degradation of PSCs as a result of mobile ionic dopants.[11] Perovskite solar cells (PSCs) with an inverted architecture (p–i–n)—in which a transparent and robust electron transporter layer (ETL) is deposited on top of perovskite—are an excellent choice for the fabrication of perovskite:silicon tandems.
Unfortunately, state-of-art-inverted PSCs with inorganic HTLs suffer from low efficiency: the highest certified PCE of inverted PSCs is 19.2%,\textsuperscript{12} fully five absolute power points lower than the best noninverted PSCs.\textsuperscript{7} Furthermore, the operational stability of efficient inverted PSCs has, until now, been less than 20 h under continuous operation.\textsuperscript{13}

To investigate inverted PSCs, we began with molecular dynamic simulations of the lattice dynamics of MAPbI\textsubscript{3} (MA is methylamine) perovskite on a NiO surface: we observed that the lattice mismatch results in structural disorder at the interface. This favors the formation of interface defects which result in carrier recombination at the interface. To reduce interfacial defects, we introduced a secondary amine, dimethylamine (DMA), to partially replace methylamine (MA) in the perovskite structure. The addition of DMA increases the rigidity of the perovskite structure and improves the lattice match, thereby reducing lattice disorder at the perovskite/NiO interface and suppressing the formation of defects.

We then fabricated inverted PSCs in which the HTL is inorganic NiO; as a result of the DMA incorporation, the optimized devices show an in-lab PCE of 21.6% and an externally certified efficiency of 20.8%. In addition, the secondary amine weakens the hydrogen bonding between the perovskite active layer and ambient water, increasing the stability of PSCs. The encapsulated inverted PSCs retain over 80% of their initial efficiency after 800 h of continuous maximum power point (MPP) operation.

We performed density function theory (DFT) calculations and first-principles adiabatic molecular dynamics (MD) simulations to calculate the structures and properties of DMA-based perovskites.\textsuperscript{14} The average length of I–Pb bonds in MA\textsubscript{1−x}DMA\textsubscript{x}PbI\textsubscript{3} and MA\textsubscript{0.875}DMA\textsubscript{0.125}PbI\textsubscript{3} at 0 and 300 K were calculated (Figure 1a and Figure S1, Supporting Information). The change in the bond length due to thermal expansion in DMA0.125 (0.091 Å) is notably smaller than that of MA1 (0.154 Å) (Figure 1b). In addition, DMA0.125 showed decreased averaged standard deviation of the position of I and Pb atoms, indicating that DMA0.125 is more rigid than MA1 (Table S1, Supporting Information).

About molecular dynamics (AIMD) were simulated to compare the NiO (001)/MA1 (110) interface and the NiO (001)/DMA0.125 (100) interface. As shown in Figure 1f,g, once we allow the MD trajectory to progress for 5 ps, we find that the NiO (001)/MA1 (110) interface becomes significantly more disordered than the NiO (001)/DMA0.125 (100) interface. The highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals show that the states are more localized on the interface of NiO (001) and MA1 (110), indicating an increased defect density. To quantify the difference, we also calculated the radial distribution function (RDF) for the two structures. Both Pb—I and Ni—O RDFs in DMA0.125 show a higher and narrower peak (Figure S2, Supporting Information), also consistent with reduced disorder at the NiO (001)/DMA0.125 (100) interface.

We then analyzed the influence of structural stiffness on the formation energy of defects (Figure 1c and Figure S3, Supporting Information): PbI\textsubscript{2} vacancies, MAI vacancies, and antisite Pb\textsubscript{b} defects. These have been reported to lead to perovskite degradation via vacancy-assisted decomposition.\textsuperscript{15} The formation energies of the aforementioned defects in DMA0.11 are all higher than those of MA1 (Figure 1d and Table S2, Supporting Information), resulting in a lower defect density in DMA0.11. This is consistent with the interface defect simulation-based studies reported above.

MA\textsubscript{1−x}DMA\textsubscript{x}PbI\textsubscript{3} perovskite films were prepared via a one-step spin-coating method\textsuperscript{16,17} (see the Experimental Section for details) by varying the ratio of DMA:MA in the precursor solution. DMA content in the final films determined by 1H NMR agrees with that in the starting precursor solutions (Figure S4, Supporting Information). The amount of DMA present in the final films is precisely controlled, ensuring that the perovskite tolerance factor is obeyed; we believe that this is important, since uncontrolled DMA content has been associated with low PCE exhibited in previous DMA-incorporating perovskites.\textsuperscript{18,19}

We characterized the crystal structure of films with X-ray diffraction (XRD; Figure 2a,b). MA1 and DMA0.03 show two dominant diffraction peaks at 2θ of 14.1° and 28.4°, corresponding to (110) and (210) planes of tetragonal perovskite phase, respectively. As we increased the DMA:MA ratio, we observed a gradual shift of the peaks of (110) and (210) planes occur (Figure 2b), indicating phase transformation from tetragonal to cubic (Table S3, Supporting Information). When the fraction of DMA is higher than 0.3, we observed phase segregation, i.e., co-formation of 3D perovskite and 1D hexagonal DMAPbI\textsubscript{3}.\textsuperscript{20–22}

We then characterized optical properties of the samples (Figure 2c). No obvious change in the absorption spectra for x < 0.3 (Figure S7a, Supporting Information) indicates that the DMA has negligible impact on the electronic structure. The photoluminescence (PL) intensity of the optimized DMA doped film is \(\approx 2\times\) higher than that of MA1. The PL decay lifetime of the DMA0.11 film is 35 ns, much longer than that of MA1 (19 ns) (Figure 2d and Table S4, Supporting Information). The longer PL lifetime along with the higher steady-state PL of DMA0.11 indicates that the nonradiative recombination is reduced in the DMA-incorporating films, suggesting that the trap state density is reduced.\textsuperscript{23} This is consistent with the higher formation energy of the perovskite structure obtained in DFT studies.

We used electrochemical strain microscopy (ESM) to map the structural stability of films.\textsuperscript{24} Perovskite grains are clearly observed in the image (Figure S10, Supporting Information). We then investigated the ionic migration rate at grains and grain boundaries using a relaxation technique\textsuperscript{25} under a stepwise DC bias (Figure 3a,b and Figure S9, Supporting Information). The DC bias modifies the local ion distribution beneath the probe; when it is removed, the transient response enables an estimation of the ions’ diffusion rate. The relaxation times of DMA0.11 (0.55 s for grains and 0.33 s for grain boundaries) are 50% larger than that of MA1 (0.34 s for grains and 0.19 s for grain boundaries), indicating inhibited ion diffusion in DMA0.11 (Table S5, Supporting Information). To investigate the stability of perovskites, we aged perovskites under relative humidity (RH) of 80 ± 5% and tracked the evolution of the absorption spectra for over 10 days (Figure S11, Supporting Information). MA1’s optical density at 750 nm decreased to 80% of its original value over this period. In contrast, the DMA0.11 film shows no obvious decrease. We attribute the improved stability to the increased hydrophobicity
Figure 1. DFT calculation and AIMD of NiO–perovskite interfaces. 
a) Schematic of stiffness changes in different temperature for MA1 (left) and DMA0.125 (right) structure. 
b) Average Pb—I bond length changes of MA1 and DMA0.125 structure in different temperature. The smaller variation of bond length for DMA0.125 means DMA0.125 structure is stiffer than MA1 structure. 
c) Structure configurations used in DFT calculations of Pb—I antisite formation energy. 
d) The formation energies of antisite and vacancies in MA1 and DMA0.11 perovskites. 
e) The adsorption energies of water on different sites of MA1 and DMA0.125 structure. 
f,g) Interface structures after 5 ps MD simulation and corresponding HOMO and LUMO for NiO (001)/MA1 (110) (f) and NiO (001)/DMA0.125 (100) (g). For simplifying the calculation, MA1 and DMA0.125 perovskite supercells were used for MD simulation.
of DMA0.11 films, as confirmed by higher static water contact angle (Figure 3c).

To understand the increased hydrophobicity of DMA0.11, we simulated the interaction of a water molecule with the tetragonal MA1 (110) surface and cubic DMA0.125 (100) surface (Figure S13, Supporting Information), the most stable lattice planes and the growth orientation for films on NiO_x substrates. The representative water adsorption energy for MA1 and DMA0.125 are −0.49 and −0.37 eV, respectively. The distance between the water molecule and the surface of the Pb–I lattice was noticeably reduced in MA1 (d = 3.54 Å) compared to DMA0.125 (d = 4.94 Å) at this site, and similar trends were found for the other three sites (Figure 3d and Table S6, Supporting Information). This points to increased hydrophobicity in the DMA0.125 films.

We then used MA1−xDMA_xPbI_3 (x value from 0% to 15%) perovskite films as the active material for solar cells in a planar inverted architecture indium tin oxide (ITO)/NiO_x/MA1−xDMA_xPbI_3/choline chloride/C_60/bathocuproine (BCP)/Ag (Figure 4a). Here, NiO_x (30 nm) and C_60 (23 nm) serve as HTL and ETL, respectively, and a thin choline chloride layer serves as the passivation layer[26] on a 450 nm thick perovskite layer (Figure 4b).

We found that the efficiency of solar cells peaks at a DMA fraction of 0.11 (Table 1), showing an optimized PCE of 21.6%, while devices based on MA1 have a PCE of only 18.2%. The hysteresis index[27] value is reduced for DMA0.11 (Table 2), likely due to the reduction in the rate of ion migration.[28] The integrated J_sc from external quantum efficiency (EQE) measurements for MA1 and DMA0.11 are 21.5 and 22.6 mA cm^{-2} (Figure 4f), respectively, which agree well with the values seen in J–V curves.

We fabricated dozens of MA1 and DMA0.11 perovskite devices. The average PCE of DMA0.11- and MA1-based devices are 20.5% and 17.4%, respectively (Figure 4d). The stabilized PCE of 21.1% for DMA0.11 measured at MPP (V_{mp}) is consistent with the value from current J–V sweeps (Figure 4e). We summarize the PCE of PSCs using the NiO_x-based inverted structure (Table S9, Supporting Information); 21.6%, to the best of our knowledge, is the highest efficiency reported to date. We sent a device for independent certification and obtained a certified PCE of 20.8% (V_{oc} = 1.138 V, J_{sc} = 21.8 mA cm^{-2}, and FF = 83.8 %) (Figure S19, Supporting Information).

To analyze the mechanism for the enhanced efficiency of the MA1−xDMA_xPbI_3, we studied the electronic properties of the films. Due to the high defect concentration of NiO_x, devices employing NiO_x layers as an HTL typically exhibit significant carrier recombination at the interface.[29] We used dark current and electrochemical impedance spectroscopy (EIS) under dark conditions to evaluate the charge carrier recombination resistance (R_{rec}) of the devices. A semicircle in the intermediate-frequency region is associated with charge recombination at interfaces[30] between the active layer and NiO_x. The larger arc of this semicircle for the DMA0.11 device (Figure 5b) indicates a large recombination resistance, consistent with the view that car-

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**Figure 2.** Characterization of perovskite films. a) Normalized XRD spectra for the mixed MA/DMA perovskite films containing different percentages of DMA. b) Magnification of the XRD peaks on variation of the DMA content. c) UV–vis absorption and PL spectra of DMA,MA1−xPbI_3 perovskite films. d) The TRPL spectroscopy of the perovskite films.
carrier recombination between NiO\textsubscript{x} and the perovskite is reduced. Additionally, devices based on DMA0.11 exhibited a lower reverse saturation current and higher rectification ratio, indicating that interface carrier recombination is reduced as well (Figure 5a).\textsuperscript{[31]}

For devices based on both MA1 and DMA0.11, the $V_{oc}$ increased monotonically as light intensity is increased. The lower ideality factor of DMA0.11 (1.58) (1.86) (Figure 5c) indicates that the nonradiative recombination process was suppressed.\textsuperscript{[32]}

We simulate the device efficiency as a function of inter-face defect concentration using solar cell capacitance simulator modeling.\textsuperscript{[33–38]} As the interface defect concentration is decreased from $3 \times 10^{12}$ to $10^{12}$ cm\textsuperscript{-2}, the PCE increases from 18\% to 21\% (Figure 5d and Figure S20a,b, Supporting Information); a negligible change in device efficiencies is observed upon changing carrier mobility from $10^{-3}$ to $10^{-4}$ cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} (Figure S20c, Supporting Information). This is consistent with the experimental results, further indicating carrier recombination at the interface plays an important role in PCE.

We compared the stability of the solar cells based on both MA1 and DMA0.11 in different environments. MA1 retained over 90\% of their initial PCE following continuous MPP testing, without filtering of UV light, for 40 h of operation in a nitrogen atmosphere (Figure S22b, Supporting Information); whereas DMA0.11 retained its performance for 120 h. Encapsulated DMA0.11 devices maintained above 81\% of its initial performance following 800 h of continuous operation under illumination using UV-filtered light, with testing carried out in air (Figure 5f).

Figure 3. ESM relaxation studies and stability characterization of perovskite films on ITO/NiO\textsubscript{x} substrate. a,b) The experimental ESM amplitude of grain (a) and grain boundary (b) versus time for MA1 and DMA0.11 measured on ITO/NiO\textsubscript{x}/perovskite under $-2$ V bias, the time of the x-axis is a reference time. c) The static water contact angle measurement of MA1 and DMA0.11 perovskite films and normalized light absorption intensities at 750 nm of the corresponding perovskite films deposited onto NiO\textsubscript{x} substrate exposed at RH $\approx$ 80\% as a function of time. d) Water adsorption structure and adsorption model for DMA0.125 and DMA molecule (left) and MA1 and MA molecule (right). The cyan ball represents the possible water adsorption area for amino group, the purple ball represents the possible water adsorption area for iodine ion which can compete with amino group, and the gray ball represents the area for methyl group to prevent the water molecule. The radii for the cyan, purple, and gray balls are 1.7, 2.6, and 2.1 Å, respectively, corresponding to the distance from the relaxed structure of these groups with water molecule.
Devices based on DMA0.11 also exhibited enhanced air stability. When storing the devices in an ambient atmosphere with an RH of 65%, the unencapsulated MA1 devices retained only 20% of their original PCE following 3 days (Figure S22a, Supporting Information); whereas DMA0.11 retained over 60% of its original PCE after a period of 12 days. We also investigated the photostability of unencapsulated PSCs under MPP operation and continuous illumination in ambient air (RH of 65%): MA1 cells showed a rapid loss of PCE at a rate of $-0.34\% \text{ min}^{-1}$ in the linear region;\textsuperscript{[15,39]} whereas DMA0.11 degraded at $-0.087\% \text{ min}^{-1}$ (Figure 5e). This rate of degradation is slower than the best value ($-0.1\% \text{ min}^{-1}$) reported across PSCs.\textsuperscript{[15]} The improved long-term stability for the DMA0.11-based devices can be ascribed to its higher water adsorption energy, as well as lower defect densities.

By introducing the secondary amine molecule DMA, we fabricated quaternary MA$_{1-x}$DMA$_x$PbI$_3$ perovskite films for inverted structure PSCs. Compared to typical MAPbI$_3$, MA$_{1-x}$DMA$_x$PbI$_3$ demonstrated improved crystal rigidity and a lower defect density, particularly at the interface between NiO and perovskite. As a result, DMA-based PSCs showed a PCE of 21.6%, the highest efficiency reported to date, to our knowledge, among inverted PSCs. Due to the increased water repulsion of the secondary amine, MA$_{1-x}$DMA$_x$PbI$_3$-based solar cells exhibited improved operating stability, retaining 80% of their original efficiency following 800 h of continuous MPP measurement. Unencapsulated
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Table 1. Photovoltaic parameters of PSCs with different DMA concentrations.

<table>
<thead>
<tr>
<th>DMAx</th>
<th>V oc [V]</th>
<th>Jsc [mA cm^-2]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA1</td>
<td>1.062</td>
<td>22.0</td>
<td>78</td>
<td>18.2</td>
</tr>
<tr>
<td>DMA0.03</td>
<td>1.060</td>
<td>21.8</td>
<td>80</td>
<td>18.6</td>
</tr>
<tr>
<td>DMA0.07</td>
<td>1.104</td>
<td>23.2</td>
<td>82</td>
<td>20.9</td>
</tr>
<tr>
<td>DMA0.09</td>
<td>1.112</td>
<td>23.4</td>
<td>82</td>
<td>21.2</td>
</tr>
<tr>
<td>DMA0.11</td>
<td>1.116</td>
<td>23.5</td>
<td>82</td>
<td>21.6</td>
</tr>
<tr>
<td>DMA0.15</td>
<td>1.109</td>
<td>21.7</td>
<td>82</td>
<td>19.7</td>
</tr>
</tbody>
</table>

Photovoltaic parameters obtained for the best-performing cells containing MA/DMA perovskite systems measured under AM 1.5G Sun illumination.

devices retained 70% of their efficiency following 5 h MPP testing in air. The decay rate of the performance is the lowest among the reported results of all PSCs. The progress herein on inverted structure performance is relevant to silicon:perovskite tandems.

**Experimental Section**

**Materials**

Lead iodide (PbI2) and BCP were purchased from TCI. Anhydrous dimethylsulfoxide (DMSO), anhydrous dimethylformamide (DMF), anhydrous isopropanol alcohol (IPA), chlorobenzene (CB), and choline chloride were purchased from Sigma Aldrich. Methylammonium iodide (MAI) was purchased from Shanghai MaterWin New Materials Technology Co., Ltd. C60 was purchased from Xi’an Polymer Light Technology Corp. Aqueous DMA (40% in water) was purchased from Macklin. Hydriodic acid (>95% in water) was purchased from Sinopharm. All salts and solvents were used as received without further purification.

DMAI was synthesized by reacting DMA and hydriodic acid with the volume ratio of 1:1 in an ice bath for 20 min. The white precipitate was recovered by evaporating the reaction mixture at 60 °C for 20 min, then the product was purified twice by recrystallization from IPA solution with diethyl ether. The resulting DMAI was collected by filtration and dried at 60 °C overnight in a vacuum oven.

NiOx nanocrystals (NCs) were synthesized according to procedures reported elsewhere, with modifications noted herein below. Briefly, 20 mmol Ni(NO3)2·6H2O were dissolved in 20 mL of deionized (DI) water to obtain a dark green solution. Then, 4 mL NaOH solution (20 mmol) was slowly added into the solution while stirring. After being stirred for 20 min, the colloidal precipitation was thoroughly washed with DI water three times and dried at 80 °C overnight under vacuum. The obtained green powder was then calcined at 270 °C for 2 h to obtain a dark-black powder. The NiOx NCs in DI water/IPA (3/1, v/v) with a concentration of 20 mg mL^-1 were dispersed by sonication. 20 mg mL^-1 of NiOx NCs in DI water/IPA (3/1, v/v) was stirred for 1.0 h, then filtered using a 0.22 µm polyethersulfone filter.

**Solar Cell Fabrication**

The patterned ITO substrates were cleaned ultrasonically by sequentially washing with DI water bath with 2% Triton X-100 v/v, DI water, acetone, and IPA for 30 min each. Before using them, the ITO was cleaned via UVO treatment for 20 min. Then, the substrate was spin-coated with a thin layer of NiOx NCs film at room temperature without any post-treatment. Stoichiometric precursor solutions were prepared by mixing MAI, DMAI, and PbI2 in a mixture of DMF and DMSO (4:1 v/v) with MAI/DMAI gradually changing from 1.0 to 0.1, while keeping the PbI2 molarity equal to 1.30, stirred for 1 h at 70 °C, and then filtered with a 0.22 µm poly(tetrafluoroethylene) filter. The perovskite layers were then fabricated by using a one-step spin-coating procedure at 1000 rpm, 10 s, and 4000 rpm, 30 s, respectively. During the second step, 600 µL of toluene was dropped at 10 s before the process ended, and this was followed by annealing at 90 °C for 8 min. After this time, the passivation layer (choline chloride) was spin-coated at 4000 rpm for 32 s from an IPA solution (1 mg mL^-1), then annealed at 90 °C for 10 min. The n-type contact layer was formed by thermally evaporating C60 (~20 nm). Then a thin and uniform BCP layer on top of C60 was deposited by drop-casting BCP dissolved in IPA in 2 to 3 s while spinning the substrate at 6000 rpm. Finally, a 120 nm thick Ag contact was deposited on top of BCP using thermal evaporation under high vacuum (~5 × 10^-7 Torr) in an Angstrom Engineering deposition system. All fabrication steps of perovskite films and top layers were performed in an N2-purged glovebox (Vigor Glovebox, O2 < 0.1 ppm, H2O < 0.1 ppm).

**Solar Cell Characterization**

The J–V characteristics of the photovoltaic cells were obtained using a Keithley 2400 Source Meter under simulated one-sun AM 1.5G illumination (100 mW cm^-2) with a solar simulator (SS-F5-3A, Enli Tech) whose intensity was calibrated with the aid of a certified standard silicon solar cell (SRC-2020, Enli Tech). To avoid stray light, a black mask with an aperture area of 0.04 cm2 was placed on the surface of devices during measurements. The J–V curves were obtained both in reverse scan (1.2 V → −0.1 V, step 0.01 V) and forward scan (−0.1 V → 1.2 V, step 0.01 V); the delay time was 200 ms, and no device preconditioning, such as light soaking or forward voltage bias applied for long time, was applied before starting the measurement. The EQE was measured using a solar-cell-spectra-response measurement system (QE-R, Enli Tech). The Mott–Schottky analysis through capacitance–voltage measurements was collected using an Ivium electrochemical workstation at 1 kHz with the bias potential ranging from 0 to 1 V under dark conditions. The EIS analysis was performed using the Ivium electrochemical workstation at a bias of 0.9 V under dark condition with the frequency ranging from 1 00 000 to 0.01 Hz and amplitude (V) = 0.01. Aging under MPP tracking was carried out on masked devices which were mounted on a temperature-controlled box. The long-term MPP operating aging process was carried out under ambient atmosphere and 1-sun equivalent illumination provided by a white light-emitting diode (LED) light source (420–780 nm). The devices were aged by means of keeping them under maximum load under illumination. The MPP was updated every 60 s by measuring the current response to a small perturbation in potential. Additionally, a full J–V scan was taken every 120 min (at a scan rate of 100 mV s^-1 starting from reverse bias) which was used to extract the displayed parameters for the aging data.

**Other Characterization**

The XRD was measured using a Bruker D8 Advance X-ray diffractometer at room temperature using Cu-Kα radiation (λ = 1.54178 Å) at 40 kV and 40 mA. The scanning electron microscopy (SEM) images were obtained by using a JSM-7800F field-emission scanning electron microscope. The UV–vis absorption spectra were obtained using a Cary Series UV–vis–NIR Spectrophotometer (Agilent Cary 5000). The static PL spectra were obtained using HORIBA FL-3000/RM4-3000 spectrophotometer. The ultraviolet photoelectron spectroscopy (UPS) measurements were carried out with the aid of a Thermo Fisher ESCALAB 250XL; 10 V bias was applied for UPS measurements. Time-resolved PL (TRPL) decay was measured using a Horiba Fluorolog-3 Time-Correlated Single Photon Counting System; the samples were excited using a pulsed laser with a wavelength of 405 nm. NMR measurements were performed using a liquid-state Bruker Avance 500 MHz spectrometer. The ESM experiments were conducted on an Asylum Research MFP-3D AFM using NanoSensors PPP-EMF probes.
with a PtIr5 metallic coating having tip radius of 25 nm and a nominal resonance frequency of 70 kHz in N2.

**DFT Calculations:** First-principles calculations were performed within the framework of DFT using plane-wave pseudopotential methods as implemented in the Vienna Ab Initio Simulation Package. The generalized gradient approximation formulated by Perdew, Burke, and Ernzerhof was used as the exchange-correlation functional. The cutoff energies for the plane wave basis set used to expand the Kohn–Sham orbitals were 400 eV, and the electron–core interactions were described by the projector augmented wave method for the pseudo potentials. For defect formation energy calculation, a $4 \times 4 \times 4$ supercell of DMA0.11 and the corresponding size supercell of MA1 were constructed to prevent the interactions between defects.

**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.

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