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Molecular Orientation Change in Naphthalene Diimide Thin Films Induced by Removal of Thermally Cleavable Substituents

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ABSTRACT: The potential of naphthalene-1,8:4,5-tetracarboxylic diimide (NDI-H) as a transparent electron-transporting material was examined. A soluble precursor was designed and synthesized having two *tert*-butoxycarbonyl solubilizing substituents at the imide moieties. This precursor molecule, NDI-Boc, is converted to the hydrogen substituted NDI-H by heating the spin-coated precursor films. The molecular orientation during the thermal conversion of NDI-Boc to NDI-H was examined using two-dimensional grazing incidence X-ray diffraction (2D-GIXD) and p-polarized multiple-angle incidence resolution spectrometry (pMAIRS). It was revealed that, driven by the formation of intermolecular hydrogen bonds, the molecular orientation changes from tilted edge-on to face-on orientation. *In situ* 2D-GIXD measurements confirmed that the change of molecular orientation is simultaneously caused by the cleaving of the Boc substituents. Time-resolved microwave conductivity (TRMC) measurements were used to show that the resulting NDI-H film has anisotropic charge-carrier transport with preferential mobility in the direction perpendicular to the film plane. We fabricated perovskite solar cells to demonstrate that the NDI-H film effectively functions as the bottom electron-transporting layer in these devices.

INTRODUCTION

The development of charge-transporting materials is a crucial issue for the achievement of high-performance organic electronic devices such as organic field-effect transistors (OFETs),¹⁻³ organic light-emitting diodes (OLEDs),^{4,5} and organic photovoltaics (OPVs).⁶⁻⁹ According to Marcus theory, charge mobility in organic thin films is determined not only by reorganization energy (λ), but also by electronic coupling (V) between π conjugated molecules.^{10,11} The electronic coupling represents the strength of the interactions between frontier orbitals, and is at a maximum when the neighboring molecules stack together in a cofacial manner. The efficiency of charge transport materials may therefore be optimized by ordering molecules so as to maximize the electronic coupling in the direction of the current flow in the target device. In lateral organic transistors where the current flows in the plane of the film between source and drain electrodes, optimizing the molecular stacking generally requires the molecules to be oriented with the π plane perpendicular to the substrate, namely, edge-on orientation. For sandwich device structures typically used for OLEDs, OPVs, and perovskite solar cells (PSCs), the current flows through the film. Therefore, for good π -stacking in this vertical direction,

the molecular plane should be aligned flat or close to flat on the substrate, namely, face-on orientation.¹²⁻¹⁵

In optoelectronic devices, the transparency of the materials in the visible light region is also important to allow efficient light into or out from devices such as displays, lighting, solar cells and photodetectors.¹⁶ A new of high-performance solution-processable class photovoltaics, perovskite solar cells (PSCs), have recently emerged as one of the hottest topics in optoelectronic materials research. Over the past few years, the power conversion efficiencies (PCEs) of PSCs have rapidly increased from 3.8%¹⁷ to above 22%.¹⁸ PSCs are typically composed of a perovskite light-absorbing layer sandwiched by an electron-transporting layer (ETL) and a hole-transporting layer (HTL) with "regular" (a substrate coated with an electron extracting layer) or "inverted" (a substrate coated with a hole extracting layer) configurations. As for the ETL, which is needed for efficient electron extraction and hole blocking from the perovskite layer, titanium dioxide (TiO₂) is widely utilized for the regular device configuration. Fabrication of the TiO_2 layer requires high temperature sintering (> 450 °C) to obtain high crystallinity and high charge carrier mobility, however, limiting low-cost mass production and application to flexible devices.¹⁹ Organic semiconductors are promising candidates to replace conventional TiO₂, and would facilitate the manufacture of PSCs at low

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temperature process. The development of transparent organic ETLs with high mobilities is challenging, however, as in addition to a wide optical gap the following requirements should also be met:

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- 1. The lowest unoccupied molecular orbital (LUMO) energy level of the ETL should match the conduction band of the perovskite.
- 2. The material should be thermally and chemically stable.
- 3. The ETL layer should be uniform, flat, and free of pinholes.

A final and important consideration for the ETL, specific to "regular" PSC cell geometries, is chemical resistance with respect to the solvent used for the spin coating of the perovskite layer on top of the ETL. Consequently, organic n-type semiconductors showing high-performance in PSC applications are still limited.²⁰⁻²⁵

Rylene tetracarboxylic diimides, represented by naphthalene diimides (NDIs), perylene diimides (PDIs), and terrylene diimides (TDIs), have been extensively investigated as n-type materials.²⁶ They have high electron affinities, high electron mobilities, and excellent chemical and thermal stabilities. Among the many rylene diimide molecules, we decided to focus on NDIs for the applications to the transparent ETL in perovskite solar cells. NDIs are the smallest rylene diimide systems and have largest optical bandgap. In thin films of NDI with alkyl substituent groups at the imide moieties, the molecules stand vertically with respect to the substrate plane and show high in-plane electron mobility in OFET devices.^{27,28} Kido, Yokoyama, Sasabe and co-workers have reported that the weak CH…N hydrogen bonds between pyridine rings can enhance the face-on orientation in the vacuum-deposited film for OLED applications.²⁹⁻³¹ Encouraged by these findings, we decided to examine NDI with hydrogen atoms at the imide moieties (NDI-H). In this molecule, the imide group can work as N-H--O intermolecular hydrogen bond sites.32,33 NDI-H has not been investigated as an electron-transporting material after a single early report indicating moderate in-plane mobility.34 If directed face-on orientation could be induced by two-dimensional sheet-like structures linked by an intermolecular hydrogen bonds network, then we can expect that NDI-H may show high out-of-plane electron mobility and thus function as an effective ETL in planar device structures such as PSCs. (Figure 1a).

Without solubilizing groups, NDI-H is expected to have very low solubility. While this is a desirable trait in terms of solvent resistance in the solid state, it significantly hinders the solution processability. Though the introduction of long alkyl chains is a common approach to gain solubility, it often inhibits the dense packing of molecules.^{35,36} To obtain solution processable films, therefore, thermally cleavable solubilizing groups are introduced.³⁷⁻⁴⁶ An NDI precursor was synthesized bearing *tert*-butoxycarbonyl (Boc) as removable solubilizing groups. Boc can be thermally cleaved with the formation of carbon dioxide and isobutene, hence NDI-H thin films can be obtained by first spin coating the precursor, designated NDI-Boc, and then heating the precursor film (Figure 1b). Whether the orientation of NDI-Boc precursor influences the orientation of the annealed NDI-H film is an interesting question which has not been explored. In order to study the NDI molecular packing structure before and after removal of the solubilizing groups, the molecular orientation during the thermal conversion of NDI-Boc to NDI-H in thin films was examined using two complementary techniques; twodimensional grazing incidence X-ray diffraction (2D-GIXD),47 which is sensitive to crystalline regions only, and p-polarized multiple-angle incidence resolution spectrometry (pMAIRS), which returns information about the ensemble average including amorphous regions.48-50

To our surprise, 2D-GIXD and pMAIRS revealed that the molecular orientation of NDI-Boc thin film changes from tilted edge-on to face-on orientation during the thermal conversion process. Time-resolved microwave conductivity (TRMC) measurements^{51,52} confirm that the resulting NDI-H film has anisotropic charge-carrier transport with a preferential mobility in the perpendicular direction to the film plane. Finally, we fabricated perovskite solar cells to demonstrate that the NDI-H film can be used as the bottom electrontransporting layer in these devices.



Figure 1. (a) Schematic images of the two-dimensional hydrogen bonds network of NDI-H, and (b) deposition of NDI-H thin film by spin-coating of precursor material and thermal conversion.

RESULTS AND DISCUSSION

Boc-protected naphthalene diimide (NDI-Boc) was synthesized in two steps from commercially available naphthalene tetracarboxylic dianhydride (NTCDA) (Scheme 1). The treatment of NTCDA with aqueous

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ammonia gave hydrogen substituted naphthalene diimide (NDI-H) in 86% yield.⁵³ Boc groups were introduced by the reaction of NDI-H with di-*tert*-butyl dicarbonate (Boc₂O) using *N*,*N*-dimethyl-4-aminopyridine (DMAP) as a catalyst,⁵⁴ giving the Boc-protected naphthalene diimide (NDI-Boc) in 66% yield. Single crystals of NDI-Boc were obtained from slow diffusion of ethyl acetate into a solution in chloroform. The NDI-Boc has a C_i symmetry where the *tert*-butyl groups in Boc moiety exist in the opposite side of the NDI plane, and exhibited herringbone packing structure (Figure S1).



Scheme 1. Synthesis of Boc-protected NDI. Reagents/conditions: i) NH_3 aq., rt, 8 h, 86%; ii) Boc_2O (3.0 equiv), DMAP (20 mol%), CH_2Cl_2 , rt, 8 h, 66%.

The temperature at which the Boc groups are cleaved in the bulk material was investigated by thermogravimetric analysis (TGA). Upon heating, a weight loss of 42.7% was observed at the onset of 187 °C and the end point of 194 °C (Figure 2a). The weight loss corresponds to the theoretical value for two Boc groups (42.9%), indicating the simultaneous elimination of both protecting groups. The Boc groups start to eliminate at ~180 °C, suggesting that the thermal conversion of NDI-Boc to NDI-H in the film state would be possible at this temperature given sufficient time (Figure 2a, inset). NDI-H meanwhile has high thermal stability with a decomposition temperature of 374 °C.

The effect of the thermal conversion on the film properties was characterized by several methods. For NDI-Boc films prepared by the spin-coating of NDI-Boc solution in chloroform on a quartz substrate, UV-Vis absorption spectra were measured before and after annealing the substrate at 180 °C for 30 minutes. The absorption maximum was slightly red-shifted from 390 nm to 401 mm (Figure 2b). It was also noted that the film thickness estimated by a stylus-based surface profiler decreased from ca. 80 nm to ca. 40 nm. Full conversion to NDI-H at this condition could also be confirmed by IR spectrometry, as will be discussed later.



Figure 2. (a) Thermogravimetric analysis of NDI-Boc under nitrogen atmosphere with the rate of 2 °C min⁻¹, and (b) absorption spectra of the spin-coated film of NDI-Boc on a quartz substrate before and after thermal conversion to NDI-H.

Information about the molecular orientation was obtained by analyzing the crystal orientation with twodimensional grazing incidence X-ray diffraction (2D-GIXD).⁴⁷ We first checked the molecular orientation on a Si(100) substrate since it has low roughness and shows no background diffractions. Spin-coated films of NDI-Boc on the Si(100) substrate show diffraction patterns which can be assigned to the single crystal structure of NDI-Boc (Figure 3a, top). 100 and 200 peaks were observed along the $\sim q_z$ axis, indicating that the NDI-Boc molecules align with the long axis perpendicular to the substrate with a tilt angle of ca. 32° from the normal, namely, tilted edge-on orientation (Figure 3b, top). The estimated *d*-spacing of 14.9 Å is comparable to the value in the crystal structure (15.1 Å).

After the thermal cleavage of Boc groups in the film by annealing at 180 °C for 30 minutes, surprisingly, the molecular orientation changed drastically. The peak at q_z ~2.0 Å⁻¹ is assignable to the 11⁻₂ peak from the π - π stacking structure (Figure 3a, middle), suggesting the face-on orientation of NDI-H (Figure 3b, middle). The estimated π - π stacking distance of 3.1 Å corresponds to the value in the crystal structure (3.1 Å).³² We also prepared the film of NDI-H by vacuum deposition for comparison. The

vacuum-deposited NDI-H film shows the similar

diffraction patterns, suggesting that here again the faceon orientation is predominant (Figure 3a, bottom). The NDI-H film prepared by thermal conversion was found to have higher crystallinity than the vacuum-deposited film, judging from the more distinct 002 and 110 diffractions.



Figure 3. Crystal orientation analysis on the thin film of NDI-Boc, NDI-H by thermal conversion, and NDI-H by vacuum deposition on Si(100) substrates. (a) 2D-GIXD images and (b) corresponding crystal structures.

A question arises with respect to the relative timing of the molecular rearrangement and the bond cleavage. Three possibilities are considered; (i) molecular orientation of NDI-Boc changes before the cleavage of Boc, (ii) face-on orientation forms immediately after the cleavage of Boc group, or (iii) edge-on oriented NDI-H forms as an intermediate state and it changes to face-on orientation only during the final stages of the annealing process. To address this question, we carried out in situ 2D-GIXD measurement by sequentially raising the temperature of the NDI-Boc thin film from room temperature to 120 °C, 140 °C, 160 °C, and finally 180 °C for every 10 minutes (Figure 4). At 120 °C, no change of molecular orientation was observed for NDI-Boc films (Figure 4b). Samples after annealing at 140 °C and 160 °C were found to be composed of edge-on oriented NDI-Boc

and face-on oriented NDI-H and did not contain edge-on oriented NDI-H (Figure 4c and 4d). These observations clearly refute the first and third possibilities, indicating instead that the change of molecular orientation from tilted edge-on to face-on directly coincides with the conversion process from NDI-Boc to NDI-H.



Figure 4. *In situ* 2D-GIXD measurements during the thermal conversion of NDI-Boc to NDI-H. 2D-GIXD images (a) before annealing, after annealing at (b) 120 °C for 10 min, (c) 140 °C for 10 min, (d) 160 °C for 10 min, and (e) 180 °C for 10 min.

The molecular orientation in the thin film can be affected by the substrate. To confirm that molecular orientation in actual devices conforms to the films grown on silicon substrates, 2D-GIXD measurements were also taken for NDI-Boc and NDI-H films on ITO and ITO/polyethylenimine ethoxylated (PEIE). (See Figure 8 for the device structure.) Though the peak intensity was weakened, similar molecular orientation was observed on ITO or ITO/PEIE (Figure S₂).

The molecular orientation of the thin films was further investigated by p-polarized multiple-angle incidence resolution spectrometry (pMAIRS), a powerful technique to discuss the molecular structure regardless of the crystallinity of the films.^{48–50} In the spin-coated film of NDI-Boc on the Si(100) substrate, three bands are

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observed in the carbonyl region (Figure 5, top). The C=O stretching vibration band of the Boc group appears at the highest wavenumber of 1771 cm⁻¹, whereas the bands at 1719 cm⁻¹ and 1681 cm⁻¹ can be assigned to the symmetric and antisymmetric C=O stretching vibration modes of the imide group, respectively.³³ The symmetric C=O stretching vibration (v_s (C=O)) band appears stronger in the OP (out-of-plane) spectrum than that in the IP (inplane) spectrum. Considering that the transition moment of v_s (C=O) mode is in the direction of the long axis, this indicates that the NDI-Boc molecules stand on the substrate in the direction of the long axis. This observation is in good general agreement with the 2D-GIXD results.

After annealing the substrate at 180 °C for 30 minutes, the IR spectra changed dramatically. The disappearance of the peak originating from the Boc group (1771 cm⁻¹) confirms the complete conversion to NDI-H (Figure 5, middle). The v_s (C=O) band appears at a different wavenumber in the IP spectrum (1700 cm⁻¹) and OP spectrum (1716 cm⁻¹). This can be explained by transverse optic (TO)-longitudinal optic (LO) splitting caused by the anomalous dispersion of the refractive index, which makes this band unsuitable for structural characterization (Figure S₃).^{55,56} Instead, another useful band of C-H outof-plane bending vibration (γ (C-H)) was used. The γ (C-H) band at 768 cm⁻¹ appears stronger in the OP spectrum than that in the IP spectrum. As the transition moment of the γ (C-H) mode is perpendicular to the molecular plane, this suggests that NDI-H adopts face-on orientation to the substrate (Figure 5, middle). Similarly, the vacuumdeposited film of NDI-H showed the predominant face-on orientation (Figure 5, bottom).

The effect of the N–H···O hydrogen bonds on the IR spectrum of NDI-H powder samples was discussed previously in a report by Seydou and coworkers.³³ They found that the N–H out-of-plane bending mode (χ (N–H)) of 864 cm⁻¹ was broadened and blue-shifted relative to the isolated molecule (710 cm⁻¹) and that this shift could be attributed to the formation of intermolecular hydrogen bonds. In our case, the broad χ (N–H) band appears at 872 cm⁻¹ for NDI-H thin film by thermal conversion and 875 cm⁻¹ for vacuum-deposited NDI-H. This indicates that the N–H···O hydrogen bonds were also formed in these films, and we can reasonably deduce that the formation of hydrogen bonds is the driving force for the change of thin film molecular orientation from tilted edge-on to face-on.

In Figure 6, the molecular orientation change of naphthalene diimide induced by the removal of thermally cleavable Boc groups is illustrated schematically. The removal of bulky Boc groups gives some space for molecules to change their orientation, and the preferential face-on orientation is induced bv intermolecular hydrogen bonds accompanied by the decrease of thickness. This would provide an explanation for how the molecules could change their orientation in thin films, where the molecules are thought to be immobile under the glass transition temperature.



1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 Wavenumber [cm⁻¹]

Figure 5. pMAIRS spectra of the thin film of NDI-Boc, NDI-H by thermal conversion, and NDI-H by vacuum deposition on Si(100) substrates.



Figure 6. Schematic illustration of the molecular orientation change in naphthalene diimide thin films induced by the removal of thermally cleavable Boc groups.

To gain insight into the relationship between packing structures and charge transport properties, we conducted theoretical calculations at the PW91/DZP level and evaluated the electronic coupling (*V*) for the crystal of NDI-H.³² Large *V* values (38–61 meV) were obtained for the electron transfer along the direction of π - π stacks, whereas small values were observed in other directions (1–22 meV) (Table S1). Therefore, the face-on oriented film of NDI-H is expected to show higher electron mobility in out-of-plane direction than that in in-plane direction. Time-resolved microwave conductivity (TRMC)

measurements^{51,52} were carried out to experimentally examine the charge transport anisotropy. TRMC measures the pseudo-photoconductivity ($\phi \Sigma \mu$) under an oscillating microwave electric field in the absence of contact between the semiconductors and the metal electrodes, where ϕ is the charge carrier generation efficiency and $\Sigma \mu$ is the sum of hole and electron mobilities. Anisotropy of the carrier mobility $(\Sigma \mu_{OP} / \Sigma \mu_{IP})$ can be estimated by the ratio of out-of-plane to in-plane mobility, in which ϕ is canceled. The thin film of NDI-H on quartz substrate prepared by thermal conversion showed larger $\phi \Sigma \mu_{OP}$ value of (5.8 ± 0.6) × 10⁻⁴ cm²V⁻¹s⁻¹ compared to $\phi \Sigma \mu_{IP}$ of $(2.0 \pm 0.2) \times 10^{-4} \text{ cm}^2 \text{V}^{-1}\text{s}^{-1}$, from which the anisotropy was estimated to be 2.9 ± 0.4 (Figure S4). Similarly, the vacuum-deposited NDI-H shows an anisotropy of 3.4 ± 0.5 $(\phi \Sigma \mu_{OP} = (2.0 \pm 0.2) \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}, \ \phi \Sigma \mu_{IP} = (0.59 \pm 0.5) \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ 0.06) \times 10⁻⁴ cm²V⁻¹s⁻¹). The higher absolute value of pseudo-photoconductivity in the film prepared by thermal conversion is consistent with the higher crystallinity of the film (Figure 3).57,58 In addition, the electron mobility of vacuum-deposited NDI-H film was examined by space-charge-limited current (SCLC) method (Figure S5). The mobility of NDI-H (5.1 \times 10⁻⁵

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 $\rm cm^2V^{-1}s^{-1})$ is comparable to that of NDI-based n-type polymers.^59

One concern about the thermal conversion method is that the removal of Boc groups may lead to the formation of a non-uniform film with pinholes or other morphological defects that could lead to high charge recombination rates when the material is used as the ETL in solar cell devices. The film morphology was verified by atomic force microscopy (AFM). We found that the spincoated film of NDI-Boc was composed of large grains with dimensions up to 500 nm. The root-mean-square (RMS) surface roughness was 20 nm (Figure 7a). After removing the Boc groups, the grain size decreased to ~150 nm, and the RMS roughness of the film decreased to 15 nm (Figure 7b). The thermal removal of Boc groups did not cause an increase of the surface roughness, instead the relatively large roughness of the NDI-H film (compared to 1.3 nm for the vacuum-deposited NDI-H film, see Figure 7c) is simply due to the roughness of the precursor NDI-Boc film. A precursor molecule with lower tendency to form large grains may therefore be a possible route to more uniform films.



Figure 7. AFM images of the thin film of (a) NDI-Boc, (b) NDI-H by thermal conversion, and (c) NDI-H by vacuum deposition on Si substrate.

Finally, the performance of NDI-H in the role of an electron-transporting layer was investigated. To this end, regular-type perovskite solar cells were fabricated having a configuration of ITO/polyethylenimine ethoxylated (PEIE)/NDI-H/MAPbI₂/Spiro-OMeTAD/Au (Figure 8a). A thin layer of PEIE (< 5 nm) was added as a work function modifier to reduce the resistance at ITO/NDI-H interface and facilitate ohmic contact.60 For comparison, a reference device with fullerene C60 was also fabricated under the same condition. Figure 8b shows the corresponding energy level diagram of the PSC. The LUMO and HOMO energy levels of NDI-H were estimated from the onset of the first reduction wave in cyclic voltammetry and absorption edge, respectively (Figure S6). The energy of the LUMO level of NDI-H (-4.0 eV) is close to the conduction band of MAPbI₂ (-3.9 eV). Figure 8c compares the cross-sectional scanning electron microscope (SEM) images of the devices with NDI-H from thermal conversion and vacuum deposition. The thickness of the constituent layers can be estimated to be ~40 nm for NDI-H ETL, ~450 nm for MAPbI₃ layer, and ~200 nm

for Spiro-OMeTAD HTL. Vacuum-deposited NDI-H has higher uniformity compared to NDI-H prepared by thermal conversion, as was previously observed in the thin film AFM images.

Figure 8d shows the forward scan current densityvoltage (J-V) characteristics of representative devices under AM 1.5 G irradiation (100 mW cm⁻²). The NDI-H layer prepared by thermal conversion functioned as the electron-transporting layer. The device exhibited the power conversion efficiency (PCE) of 4.8% with short circuit current density (J_{SC}) of 13.6 mA cm⁻², open circuit voltage (V_{OC}) of 0.83 V, and fill factor (FF) of 0.43 (Table 1). The device using a vacuum-deposited NDI-H layer showed a higher PCE of 10.7% with J_{SC} = 18.9 mA cm⁻², V_{OC} = 0.88 V, and FF = 0.64, which was comparable to the performance obtained with a C_{60} ETL in the same device structure (9.3%). The variation in the PCE between the NDI-H layers fabricated by thermal conversion and vacuum deposition arises primarily from the difference in the short circuit current (13.6 mA cm⁻² vs. 18.9 mA cm⁻²) and shunt resistance $(R_{\rm sh})$ (120 Ω cm² vs. 314 Ω cm²),

estimated from the slope of J-V curves near zero applied bias. Given the high surface roughness, some regions of the thermally converted NDI-H layer can be expected to be significantly thinner than the average thickness of 40 nm. A possible explanation for the smaller J_{SC} and R_{sh} is that these very thin regions have insufficient holeblocking ability, leading to an increase in the charge recombination rates. This is corroborated by the observation that the device using vacuum-deposited NDI-H with a smaller thickness of 20 nm showed decreased J_{SC} and R_{sh} compared to that with 40 nm layer (Figure S7, Table S2).

Figure 8e shows the incident photon to current conversion efficiency (IPCE) spectra. The PSC device using vacuum-deposited NDI-H showed relatively high IPCE of 0.7 to 0.8 in the visible region, though a drop of quantum efficiency was observed at the near UV region. Referring back to the UV-Vis absorption spectrum of NDI-H (Figure 2b), we can see that this drop of IPCE is due to the absorption of incident light by the NDI-H layer. *J*_{SC} could be increased further, therefore, by using an ETL with a shorter absorption wavelength.



Figure 8. Fabrication of perovskite solar cell using NDI-H as an electron transport layer. (a) Device structure, (b) energy level diagram, (c) cross-sectional SEM images of solar cells, (d) forward scan *J*–*V* characteristics, and (e) incident photon to current conversion efficiency (IPCE) spectra.

Table 1. Photovoltaic Parameters of PSCs using NDI-H or C_{60} as an Electron Transport Layer, Derived from Forward Scan *J–V* Characteristics

	$J_{\rm SC} [{\rm mAcm^{-2}}]$	$V_{\rm OC}$ [V]	FF	PCE [%]	$R_{\rm sh} \left[\Omega {\rm cm^2}\right]$
NDI-H (thermal conversion)	13.6	0.83	0.43	4.8	120
NDI-H (vacuum deposition)	18.9	0.88	0.64	10.7	311
C ₆₀	16.9	0.95	0.58	9.3	152

CONCLUSIONS

In summary, naphthalene diimide (NDI-H) films with face-on orientation to the substrate were successfully prepared by heating the spin-coated film of the NDI-Boc precursor compound. The initial edge-on orientation of NDI-Boc changed to a face-on orientation during thermal cleavage of the Boc groups. Anisotropic charge-carrier-transport up to 3:1 was observed in the NDI-H film. The NDI-H layers prepared by thermal conversion were demonstrated to function as the transparent electron transport layer in regular-type perovskite solar cells, while the device using vacuum-deposited NDI-H showed comparable performance to a C_{60} -based device. Near-UV absorption by NDI-H reduces the amount of light absorbed by the perovskite layer, causing a proportionate loss in conversion efficiency. The development of electron transport materials having shorter absorption wavelength is currently in progress in our laboratory, and results will be reported in due course.

ASSOCIATED CONTENT

Supporting Information

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The Supporting Information is available free of charge on the ACS Publications website.

Experimental details and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Anthony, J. E. The Larger Acenes: Versatile Organic Semiconductors. *Angew. Chem., Int. Ed.* **2008**, 47, 452–483.
- (2) Klauk, H. Organic Thin-Film Transistors. *Chem. Soc. Rev.* 2010, 39, 2643-2666.

- (3) Wang, C.; Dong, H.; Hu, W.; Liu, Y.; Zhu, D. Semiconducting π-Conjugated Systems in Field-Effect Transistors: A Material Odyssey of Organic Electronics. *Chem. Rev.* 2012, 112, 2208–2267.
- (4) Shirota, Y.; Kageyama, H. Charge Carrier Transporting Molecular Materials and Their Applications in Devices. *Chem. Rev.* 2007, *107*, 953–1010.
- (5) Xiao, L.; Chen, Z.; Qu, B.; Luo, J.; Kong, S.; Gong, Q.; Kido, J. Recent Progresses on Materials for Electrophosphorescent Organic Light-Emitting Devices. *Adv. Mater.* 2011, 23, 926– 952.
- Walker, B.; Kim, C.; Nguyen, T. Q. Small Molecule Solution-Processed Bulk Heterojunction Solar Cells. *Chem. Mater.* 2011, 23, 470–482.
- (7) Facchetti, A. π-Conjugated Polymers for Organic Electronics and Photovoltaic Cell Applications. *Chem. Mater.* 2011, 23, 733–758.
- (8) Mishra, A.; Bäuerle, P. Small Molecule Organic Semiconductors on the Move: Promises for Future Solar Energy Technology. Angew. Chem., Int. Ed. 2012, 51, 2020– 2067.
- Kularatne, R. S.; Magurudeniya, H. D.; Sista, P.; Biewer, M. C.; Stefan, M. C. Donor-Acceptor Semiconducting Polymers for Organic Solar Cells. J. Polym. Sci. Part A Polym. Chem. 2013, 51, 743–768.
- (10) Marcus, R. A. On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I. J. Chem. Phys. 1956, 24, 966–978.
- (11) Marcus, R. A.; Sustin, N. Electron Transfers in Chemistry and Biology. *Biochem. Biophys. Acta* **1985**, *81*, 265–322.
- (12) Osaka, I.; Takimiya, K. Backbone Orientation in Semiconducting Polymers. *Polymer* **2015**, *59*, A1–A15.
- (13) Yokoyama, D. Molecular Orientation in Small-Molecule Organic Light-Emitting Diodes. J. Mater. Chem. 2011, 21, 19187–19202.
- (14) Wakamiya, A.; Nishimura, H.; Fukushima, T.; Suzuki, F.; Saeki, A.; Seki, S.; Osaka, I.; Sasamori, T.; Murata, M.; Murata, Y.; Kaji, H. On-Top π-Stacking of Quasiplanar Molecules in Hole-Transporting Materials: Inducing Anisotropic Carrier Mobility in Amorphous Films. *Angew. Chem., Int. Ed.* 2014, 53, 5800–5804.
- (15) Nishimura, H.; Ishida, N.; Shimazaki, A.; Wakamiya, A.; Saeki, A.; Scott, L. T.; Murata, Y. Hole-Transporting Materials with a Two-Dimensionally Expanded π -System around an Azulene Core for Efficient Perovskite Solar Cells. J. Am. Chem. Soc. **2015**, *137*, 15656–15659.
- (16) Nishimura, H.; Hasegawa, Y.; Wakamiya, A.; Murata, Y. Development of Transparent Organic Hole-Transporting Materials Using Partially Oxygen-Bridged Triphenylamine Skeletons. Chem. Lett. 2017, 46, 817–820.
- (17) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. J. Am. Chem. Soc. 2009, 131, 6050– 6051.
- (18) Green, M. A.; Hishikawa, Y.; Dunlop, E. D.; Levi, D. H.; Hohl-Ebinger, J.; Ho-Baillie, A. W. Y. Solar Cell Efficiency Tables (Version 52). Prog. Photovoltaics Res. Appl. 2018, 26, 427–436.
- (19) Wu, W.-Q.; Chen, D.; Caruso, R. A.; Cheng, Y.-B. Recent Progress in Hybrid Perovskite Solar Cells Based on n-Type Materials. J. Mater. Chem. A 2017, 5, 10092–10109.
- (20) Kim, J. H.; Chueh, C. C.; Williams, S. T.; Jen, A. K. Y. Room-Temperature, Solution-Processable Organic Electron Extraction Layer for High-Performance Planar Heterojunction Perovskite Solar Cells. *Nanoscale* 2015, 7, 17343–17349.
- (21) Yoon, H.; Kang, S. M.; Lee, J. K.; Choi, M. Hysteresis-Free Low-Temperature-Processed Planar Perovskite Solar Cells with 19.1% Efficiency. *Energy Environ. Sci.* 2016, *9*, 2262– 2266.

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57 58 59

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- (22) Zhang, H.; Xue, L.; Han, J.; Fu, Y. Q.; Shen, Y.; Zhang, Z.; Li, Y.; Wang, M. New Generation Perovskite Solar Cells with Solution-Processed Amino-Substituted Perylene Diimide Derivative as Electron-Transport Layer. J. Mater. Chem. A 2016, 4, 8724–8733.
- (23) Zhu, Z.; Xu, J. Q.; Chueh, C. C.; Liu, H.; Li, Z.; Li, X.; Chen, H.; Jen, A. K. Y. A Low-Temperature, Solution-Processable Organic Electron-Transporting Layer Based on Planar Coronene for High-Performance Conventional Perovskite Solar Cells. Adv. Mater. 2016, 28, 10786–10793.
- (24) Zhang, M.; Zhu, J.; Liu, K.; Zheng, G.; Zhao, G.; Li, L.; Meng, Y.; Guo, T.; Zhou, H.; Zhan, X. A Low Temperature Processed Fused-Ring Electron Transport Material for Efficient Planar Perovskite Solar Cells. J. Mater. Chem. A 2017, 5, 24820-24825.
- (25) Li, D.; Sun, C.; Li, H.; Shi, H.; Shai, X.; Sun, Q.; Han, J.; Shen, Y.; Yip, H. L.; Huang, F.; Wang, M. Amino-Functionalized Conjugated Polymer Electron Transport Layers Enhance the UV-Photostability of Planar Heterojunction Perovskite Solar Cells. *Chem. Sci.* 2017, *8*, 4587-4594.
- (26) Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. Rylene and Related Diimides for Organic Electronics. *Adv. Mater.* 2011, 23, 268–284.
- (27) Katz, H. E.; Johnson, J.; Lovinger, A. J.; Li, W. Naphthalenetetracarboxylic Diimide-Based n-Channel Transistor Semiconductors: Structural Variation and Thiol-Enhanced Gold Contacts. J. Am. Chem. Soc. 2000, 122, 7787– 7792.
- (28) Shukla, D.; Nelson, S. F.; Freeman, D. C.; Rajeswaran, M.; Ahearn, W. G.; Meyer, D. M.; Carey, J. T. Thin-Film Morphology Control in Naphthalene-Diimide-Based Semiconductors: High Mobility n-Type Semiconductor for Organic Thin-Film Transistors. *Chem. Mater.* 2008, 20, 7486–7491.
- Yokoyama, D.; Sasabe, H.; Furukawa, Y.; Adachi, C.; Kido, J.
 Molecular Stacking Induced by Intermolecular C-H…N
 Hydrogen Bonds Leading to High Carrier Mobility in
 Vacuum-Deposited Organic Films. Adv. Funct. Mater. 2011, 21, 1375–1382.
- (30) Watanabe, Y.; Sasabe, H.; Yokoyama, D.; Beppu, T.; Katagiri, H.; Pu, Y. J.; Kido, J. Simultaneous Manipulation of Intramolecular and Intermolecular Hydrogen Bonds in n-Type Organic Semiconductor Layers: Realization of Horizontal Orientation in OLEDs. Adv. Opt. Mater. 2015, 3, 769–773.
- (31) Watanabe, Y.; Sasabe, H.; Yokoyama, D.; Beppu, T.; Katagiri, H.; Kido, J. Synthesis, Properties, and OLED Characteristics of 2,2'-Bipyridine-Based Electron-Transport Materials: The Synergistic Effect of Molecular Shape Anisotropy and a Weak Hydrogen-Bonding Network on Molecular Orientation. J. Mater. Chem. C 2016, 4, 3699– 3704.
- Keeling, D. L.; Oxtoby, N. S.; Wilson, C.; Humphry, M. J.; Champness, N. R.; Beton, P. H. Assembly and Processing of Hydrogen Bond Induced Supramolecular Nanostructures. *Nano Lett.* 2003, 3, 9–12.
- (33) Seydou, M.; Teyssandier, J.; Battaglini, N.; Kenfack, G. T.; Lang, P.; Tielens, F.; Maurel, F.; Diawara, B. Characterization of NTCDI Supra-Molecular Networks on Au(111); Combining STM, IR and DFT Calculations. *RSC Adv.* 2014, 4, 25698–25708.
- Laquindanum, J. G.; Katz, H. E.; Dodabalapur, A.; Lovinger,
 A. J. n-Channel Organic Transistor Materials Based on Naphthalene Frameworks. J. Am. Chem. Soc. 1996, 118, 11331– 11332.
 - (35) Song, C. E.; Kim, Y. J.; Suranagi, S. R.; Kini, G. P.; Park, S.;
 Lee, S. K.; Shin, W. S.; Moon, S. J.; Kang, I. N.; Park, C. E.;
 Lee, J. C. Impact of the Crystalline Packing Structures on

Charge Transport and Recombination via Alkyl Chain Tunability of DPP-Based Small Molecules in Bulk Heterojunction Solar Cells. *ACS Appl. Mater. Interfaces* **2016**, *8*, 12940–12950.

- (36) Fuentes Pineda, R.; Troughton, J.; Planells, M.; Sanchez-Molina Santos, I.; Muhith, F.; Nichol, G. S.; Haque, S.; Watson, T.; Robertson, N. Effect of Alkyl Chain Length on the Properties of Triphenylamine-Based Hole Transport Materials and their Performance in Perovskite Solar Cells. *Phys. Chem. Chem. Phys.* 2018, 20, 1252–1260.
- (37) Zambounis, J. S.; Hao, Z.; Iqbal, A. Latent Pigments Activated by Heat. *Nature* **1997**, 388, 131–132.
- Liu, J.; Kadnikova, E. N.; Liu, Y.; Mcgehee, M. D.; Fréchet, J. M. J. Polythiophene Containing Thermally Removable Solubilizing Groups Enhances the Interface and the Performance of Polymer-Titania Hybrid Solar Cells. J. Am. Chem. Soc. 2004, 126, 9486–9487.
- (39) Petersen, M. H.; Gevorgyan, S. A.; Frederik, C. K. Thermocleavable Low Band Gap Polymers and Solar Cells Therefrom with Remarkable Stability toward Oxygen. *Macromolecules* 2008, *41*, 8986–8994.
- (40) Gevorgyan, S. A.; Krebs, F. C. Bulk Heterojunctions Based on Native Polythiophene. *Chem. Mater.* 2008, 20, 4386– 4390.
- Jørgensen, M.; Hagemann, O.; Alstrup, J.; Krebs, F. C. Thermo-Cleavable Solvents for Printing Conjugated Polymers: Application in Polymer Solar Cells. Sol. Energy Mater. Sol. Cells 2009, 93, 413–421.
- (42) Helgesen, M.; Gevorgyan, S. A.; Krebs, F. C.; Janssen, R. A. J. Substituted 2,1,3-Benzothiadiazole- and Thiophene-Based Polymers for Solar Cells – Introducing a New Thermocleavable Precursor. *Chem. Mater.* 2009, 21, 4669– 4675.
- (43) Chen, T. L.; Chen, J. J. A.; Catane, L.; Ma, B. Fully Solution Processed p-i-n Organic Solar Cells with an Industrial Pigment - Quinacridone. Org. Electron. 2011, 12, 1126–1131.
- (44) Brusso, J. L.; Lilliedal, M. R.; Holdcroft, S. π-Conjugated Polymers with Thermocleavable Substituents for Use as Active Layers in Organic Photovoltaics. *Polym. Chem.* 2011, 2, 175–180.
- (45) Zuniga, C. A.; Abdallah, J.; Haske, W.; Zhang, Y.; Coropceanu, I.; Barlow, S.; Kippelen, B.; Marder, S. R. Crosslinking Using Rapid Thermal Processing for the Fabrication of Efficient Solution-Processed Phosphorescent Organic Light-Emitting Diodes. *Adv. Mater.* 2013, 25, 1739– 1744.
- (46) Hillebrandt, S.; Adermann, T.; Alt, M.; Schinke, J.; Glaser, T.; Mankel, E.; Hernandez-Sosa, G.; Jaegermann, W.; Lemmer, U.; Pucci, A.; Kowalsky, W.; Müllen, K.; Lovrincic, R.; Hamburger, M. Naphthalene Tetracarboxydiimide-Based n-Type Polymers with Removable Solubility via Thermally Cleavable Side Chains. ACS Appl. Mater. Interfaces 2016, 8, 4940–4945.
- (47) Rivnay, J.; Mannsfeld, S. C. B.; Miller, C. E.; Salleo, A.; Toney, M. F. Quantitative Determination of Organic Semiconductor Microstructure from the Molecular to Device Scale. *Chem. Rev.* 2012, *112*, 5488–5519.
- (48) Hasegawa, T. A Novel Measurement Technique of Pure Out-of-Plane Vibrational Modes in Thin Films on a Nonmetallic Material with No Polarizer. J. Phys. Chem. B 2002, 106, 4112–4115.
- (49) Hasegawa, T. Advanced Multiple-Angle Incidence Resolution Spectrometry for Thin-Layer Analysis on a Low-Refractive-Index Substrate. *Anal. Chem.* 2007, 79, 4385– 4389.
- (50) Shioya, N.; Norimoto, S.; Izumi, N.; Hada, M.; Shimoaka, T.; Hasegawa, T. Optimal Experimental Condition of IR pMAIRS Calibrated by Using an Optically Isotropic Thin Film Exhibiting the Berreman Effect. *Appl. Spectrosc.* 2017, 71, 901–910.

- (51) Saeki, A.; Seki, S.; Takenobu, T.; Iwasa, Y.; Tagawa, S. Mobility and Dynamics of Charge Carriers in Rubrene Single Crystals Studied by Flash-Photolysis Microwave Conductivity and Optical Spectroscopy. *Adv. Mater.* 2008, 20, 920–923.
- (52) Saeki, A.; Yoshikawa, S.; Tsuji, M.; Koizumi, Y.; Ide, M.; Vijayakumar, C.; Seki, S. A Versatile Approach to Organic Photovoltaics Evaluation Using White Light Pulse and Microwave Conductivity. J. Am. Chem. Soc. 2012, 134, 19035– 19042.
- (53) Sotiriou-Leventis, C.; Mao, Z. A Facile Synthesis of 2,7-Diazapyrene. J. Heterocycl. Chem. 2000, 37, 1665–1667.
- (54) Sengoku, T.; Murata, Y.; Aso, Y.; Kawakami, A.; Inuzuka, T.; Sakamoto, M.; Takahashi, M.; Yoda, H. Indium-Catalyzed Amide Allylation of *N*-Carbonyl Imides: Formation of Azaspiro-γ-Lactones via Ring Opening-Reclosure. *Org. Lett.* 2015, 17, 5846–5849.
- (55) Berreman, D. W. Infrared Absorption at Longitudinal Optic Frequency in Cubic Crystal Films. *Phys. Rev.* 1963, 130, 2193– 2198.
- (56) Yamamoto, K.; Masui, A. TO-LO Splitting in Infrared Spectra of Thin Films. *Appl. Spectrosc.* 1996, 50, 759–763.

- (57) Yoshikawa, S.; Saeki, A.; Saito, M.; Osaka, I.; Seki, S. On the Role of Local Charge Carrier Mobility in the Charge Separation Mechanism of Organic Photovoltaics. *Phys. Chem. Chem. Phys.* 2015, *17*, 17778–17784.
- (58) Shimata, Y.; Ide, M.; Tashiro, M.; Katouda, M.; Imamura, Y.; Saeki, A. Charge Dynamics at Heterojunction between Face-on/Edge-on PCPDTBT and PCBM Bilayer: Interplay of Donor/Acceptor Distance and Local Charge Carrier Mobility. J. Phys. Chem. C 2016, 120, 17887–17897.
- (59) Shen, G.; Li, X.; Wu, X.; Wang, Y.; Shan, H.; Xu, J.; Liu, X.; Xu, Z. X.; Chen, F.; Chen, Z. K. Naphthalene Tetracarboxylic Diimide (NDI)-Based Polymer Solar Cells Processed by Non-Halogenated Solvents. Org. Electron. 2017, 46, 203–210.
- (6o) Zhou, Y.; Fuentes-hernandez, C.; Shim, J.; Meyer, J.; Giordano, A. J.; Li, H.; Winget, P.; Papadopoulos, T.; Cheun, H.; Kim, J.; Fenoll, M.; Dindar, A.; Haske, W.; Najafabadi, E.; Khan, T. M.; Sojoudi, H.; Barlow, S.; Graham, S.; Brédas, J. L.; Marder, S. R.; Kahn, A.; Kippelen, B. A Universal Method to Produce Low–Work Function Electrodes for Organic Electronics. *Science* 2012, 336, 327–332.

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