Separated Crystallization of Donor and Acceptor in Oligo(*p*-phenylenevinylene)-Naphthalenediimide Dyad Films

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RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

ABSTRACT: A dyad molecule was synthesized, with oligo(*p*-phenylenevinylene) (OPV) as the electron donor and naphthalene diimide (NDI) as the acceptor. The optical, thermal, and X-ray

diffraction measurements of the film structure showed that the OPV and NDI moieties of the dyad crystallized separately in the spin-coated films. This is in striking contrast to the previously reported OPV and C₇₀ fullerene dyad, in which the introduction of C₇₀ severely disrupted the OPV packing. The separated crystallization in the OPV-NDI dyad was attributed to the planar shape of the acceptor and the differences in the crystalline structures of planar NDI and rod-like OPV.

Keywords: Dyad molecule, Crystallization, X-ray diffraction, Organic Solar Cells

1. Introduction

Precise control of the ordering and alignment of π -conjugated molecules in solid films through molecular design is important because nanoscale film morphology strongly affects the efficiency of many organic electronic devices.¹⁻³ This is particularly important for efficient organic solar cells (OSCs) because the electron donor and acceptor molecules in the films must form separate domains on the scale of several tens of nanometers for efficient simultaneous charge generation and transport.⁴ To obtain ideal nanomorphologies for the donor and acceptor in the active layer of OSCs, a solution containing a mixture of the two compounds is often used.⁵⁻⁶ The fabrication conditions, including solvents,⁷ thermal annealing,⁸ and additives,⁹ have been optimized. Several groups have achieved high power conversion efficiency (PCE) greater than 8% in mixed bulk heterojunction (BHJ) OSCs¹⁰⁻¹¹ with fullerene derivatives as the acceptor. However, the phase-separated nanostructures are not necessarily well-controlled and BHJ systems often suffer from undesirable large aggregations of either the donors or the fullerenes, which reduces the efficiency of the charge separation. This problem could also reduce the reproducibility of the device performance. In addition, the mixed structures are often not in a thermodynamically stable state and phase separation could occur after operation at high temperatures for a long time.¹²⁻¹³ This morphological change reduced the device performance substantially.

Dyad molecules, in which the D and A moieties are covalently attached to each other, have been

intensively studied for controlling the donor/acceptor (D/A) nanomorphology.¹⁴ The efficiency has been improved from about 0.1% in early studies to more than 1% recently.¹⁵⁻¹⁷ We reported that a dyad based on oligo(*p*-phenylenevinylene) (OPV) and C₇₀ fullerene showed a record PCE of 1.92% and good morphological and device stability at high temperatures.¹⁸ However, the PCEs of dyad-based OSCs is still much lower than those of BHJ OSCs.^{10-11, 19} One problem is that the covalent bonds between the donor and the acceptor often disturb the molecular ordering of each moiety.²⁰ For example, the attachment of a fullerene to the crystalline donor significantly reduces the crystallinity,²¹ resulting in the absence of X-ray diffraction peaks.²² Because the crystallinity of both the donor and the acceptor domains could be key to achieving efficient charge transport, it would be ideal if the donor and acceptor crystallized separately in the dyad films.²³

In this study, we synthesized a new dyad molecule with OPV as the donor and naphthalene diimide (NDI) as the acceptor, connected by a long flexible hexaethylene glycol linker (Scheme 1). NDI has good electron transport properties and is often used in n-type organic field transistors.²⁴⁻²⁵ Furthermore, we expected that the planar π -plane²⁶ of NDI would not disturb the π -stacking of OPV. The structure of the dyad was determined by optical, thermal, and X-ray diffraction (XRD) measurements. OSC devices were fabricated with the dyad.

2. Experimental Section

2.1. Synthetic details

All chemicals were purchased from the chemical suppliers and used without further purification. The synthetic route to OPV (**1**) in Scheme 1 has been reported previously.²⁷ The products were characterized by ¹H NMR spectroscopy and MALDI-TOF-MS as shown in Supporting Information.

N-(2-Ethylhexyl)-*N'*-(hexane-6-carboxylic acid)-naphthalenebisimide (NDICOOH) (**2**)

6-Aminohexanoic acid (1.968 g, 15.0 mmol), 2-ethylhexylamine (2.454 mL, 15.0 mmol), anhydrous

zinc acetate (1.373 g), and anhydrous DMF (50 mL) were added to a 100 mL two-neck round-bottom flask under N₂. The reaction mixture was stirred for 1 h at 150 °C, and then 1,4,5,8-naphthalenetetracarboxylic dianhydride (2.68 g, 10.0 mmol) was added. The reaction mixture was stirred overnight at 150 °C. After cooling to room temperature, the mixture was extracted with CHCl₃. The crude product was purified by silica gel column chromatography (CHCl₃), yielding **2** as a pink solid (605 mg, 12%).

¹H NMR (CDCl₃, 300MHz): δ(ppm): 8.76 (s, 4H), 4.12-4.23 (m, 4H), 2.37-2.41 (t, 2H), 1.92-1.99 (m, 1H), 1.71-1.80 (m, 4H), 1.48-1.52 (m, 2H), 1.30-1.42 (m, 8H), 0.92-0.96 (t, 3H), 0.86-0.90 (t, 3H).

OPV-NDI dyad (**3**)

2 (57 mg, 0.117 mmol) was placed in a 50 mL two-neck round-bottom flask under N₂; then anhydrous chlorobenzene (5 mL) and thionyl chloride (1.012 mL, 14.0 mmol) were added. The reaction mixture was stirred overnight at 70 °C. The solvent was removed in vacuo and anhydrous chlorobenzene (5 mL) was added. NaH (oil dispersion 50-72%, 17.8 mg, washed with hexane prior to use) in anhydrous chlorobenzene (45 mL) was added to the mixture containing **1** (100 mg, 0.117 mmol). The reaction mixture was stirred at room temperature for 48 h and then purified by column chromatography using silica gel and CHCl₃ as eluent, yielding **3** as a yellow solid (43 mg, 28%).

¹H NMR (CDCl₃, 300MHz): δ(ppm): 8.70 (s, 4H), 7.37-7.46 (m, 14H), 6.88-7.12 (m, 12H), 4.18-4.21 (m, 4H), 4.01-4.09 (m, 4H), 3.92-3.97 (m, 5H), 3.85 (s, 6H), 3.58-3.74 (m, 20H), 2.30-2.35 (t, 2H), 1.87-1.95 (m, 1H), 1.65-1.70 (m, 4H), 1.20-1.45 (m, 10H), 0.86-0.92 (m, 6H). MALDI-TOF-MS (C₈₁H₉₀N₂O₁₅) calcd. 1331.59, found 1331.39.

2.2. Measurement

¹H NMR were measured on JNM-AL300 (JEOL). MALDI-TOF-MS spectra were measured on Ultraflex RO (Bruker Daltonics) with dithranol as the matrix. UV-vis absorption spectra were

measured on a V-670 spectrometer (JASCO). Fluorescence spectra were measured on an F-4500 fluorescence spectrophotometer (Hitachi). Cyclic voltammetry (CV) was performed on an HSV-100 automatic polarization system (Hokuto Denko) in N₂. 0.1 M Tetrabutylammomium hexafluorophosphate in anhydrous CHCl₃ was used as the supporting electrolyte. A glassy carbon working electrode, a Pt wire counter electrode, and a Ag/AgCl reference electrode were used. Differential scanning calorimetry (DSC) traces were obtained on a Thermo plus DSC8230 calorimeter (Rigaku). 2D-GIXRD patterns were measured at an incident angle of 0.12° using synchrotron radiation at beamline BL19B2 of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute. Variable temperature θ -2 θ XRD patterns were measured with a Smart Lab X-Ray diffractometer (Rigaku) with Cu K α at 45 kV and 200 mA. The sample was covered with a plastic dome (Anton Paar, transmittance of Cu K α : 73%) in a vacuum. The temperature of the stage was controlled by a TCU 150 temperature control unit (Anton Paar). Film thickness was measured by surface profilometry (Dektak 6M, ULVAC, Japan). Atomic force microscopy (AFM) images were obtained on a Nanonavi station/S-image (SII technology) operated in tapping mode. Films were prepared by spin coating CHCl₃ solutions of the OPV-NDI dyad with a total concentration of 10 mg mL⁻¹ at 2500 rpm on a glass substrate for the UV-vis absorption and fluorescence measurement, and on silicon wafers for 2D-GIXRD measurements with no thermal annealing.

2.3. Photovoltaic device preparation and measurement

An indium tin oxide (ITO)-coated glass substrate (sheet resistance: 10 Ω sq⁻¹, Geomatec) was cleaned by sequential ultra-sonication in detergent solution, water, acetone, 2-propanol, and water. The substrate was dried and then spin coated with PEDOT:PSS (H. C. Stark) at 4000 rpm. The film was dried at 150 °C under N₂ for 20 min. After cooling, the substrate was spin coated with a CHCl₃ solution of the OPV-NDI dyad with a total concentration of 10 mg mL⁻¹ at 2500 rpm. Finally, Ca (20 nm) and Al (40 nm) electrodes were evaporated onto the organic layer under high vacuum (6×10^{-4} Pa). The devices

were annealed at temperatures of 100, 130, or 160 °C for 5 min, and devices without thermal annealing were also prepared. The *J-V* characteristics of the devices were measured under simulated solar illumination (AM 1.5, 100 mW cm⁻²) from a 150 W Xe lamp (PEC-L11, Peccell Technologies) with an AM 1.5 filter. The light intensity was calibrated with a standard silicon solar cell (BS520, Bunkoh-Keiki). The active area of the devices was defined by using a 0.12 cm² photo mask. The external quantum efficiency (EQE) of the devices was measured on a Hypermonolight SM-250F system (Bunkoh-Keiki).

3. Results and discussion

3.1. Synthesis

The dyad molecule with NDI and OPV (OPV-NDI dyad) was synthesized by following Scheme 1. The synthesis of OPV was reported previously by us.²⁷ NDICOOH was synthesized by using two kinds of amines to asymmetrically convert the tetracarboxylic acid dianhydride to the diimide in one pot reaction. The symmetrically substituted diimides were removed by column chromatography. The products were characterised by ¹H NMR and MALDI-TOF-MS (Supporting Information) All the peaks in ¹H NMR of the product were assigned to NDICOOH and the ratios of the peak area were consistent with the chemical structure, besides minor unknown peaks were observed at 3.31, 3.02, 2.94 and 2.87 ppm. Peaks correspond to alpha methylene next to diimide nitrogens were composed by triplet in 4.19-4.23 ppm from 6-carboxylic acid-hexylimide and multiplet in 4.12-4.19 ppm from 2-ethylhexylimide.²⁶ OPV-NDI dyad was synthesised by esterification of OPV and NDICOOH through the formation of carboxylic acid chloride. All the peaks in ¹H NMR of the product were assigned to OPV-NDI except residual solvent and water peaks and the ratios of the peak area were consistent with the chemical structure of the dyad. MALDI-TOF-MS showed single peak corresponding to the molecular weight of the dyad. Note that possible impurity of triad which might be formed from the symmetrical dimide in previous step was not found in MALDI-TOF-MS.

3.2. Molecular properties

Absorption spectra

Figure 1a shows the UV-vis absorption spectra of the OPV-NDI dyad, OPV, and NDICOOH in CHCl_3 . OPV has an absorption peak at 420 nm and NDICOOH has three peaks at 342, 360, and 380 nm. The absorption spectrum of the OPV-NDI dyad molecule was a simple sum of the OPV and NDICOOH spectra. This represents that there is little electrical interaction in the ground state between the OPV and NDI parts of the dyad in solution. The optical band gap of the donor part was estimated from the absorption edges as 2.56 eV, which corresponds to that of OPV. The absorption spectra of the OPV-NDI dyad, OPV, and the OPV- C_{70} dyad (as a reference) thin films are shown in Figure 1b. In the pristine OPV film, the peak was red shifted to 440 nm compared with the solution spectrum and an absorption shoulder appeared around 480 nm. The red shift in the OPV absorption could be caused by *J*-aggregation, which has been observed previously.¹⁶ This peak shift and the appearance of a shoulder in the absorption of OPV was also observed in thin films of the OPV-NDI dyad and the OPV- C_{70} dyad. This indicates that donor moiety aggregated in both the OPV-NDI dyad and the OPV- C_{70} dyad films.

Fluorescence spectra

Fluorescence spectra of the OPV-NDI dyad, OPV, OPV- C_{70} dyad, and an equimolar solution of OPV and NDI in CHCl_3 are shown in Figure 2a. The solutions had a similar low absorbance of approximately 0.02 at the excitation wavelength of 420 nm to avoid aggregation and the fluorescence intensity was normalized by the absorbance. OPV showed strong fluorescence with a peak maximum at 485 nm, whereas attaching the NDI moiety significantly decreased the fluorescence intensity. This denotes that the excited state of OPV part was quenched by intramolecular charge transfer from the OPV to the NDI moiety in the dyads. In contrast, the mixture of OPV and NDICOOH showed almost the same fluorescence intensity as the OPV solution. These results reflect the proximity of the donor and

the acceptor in the OPV-NDI dyad in solution because of the hexaethylene glycol linker. The fluorescence intensity of the OPV-C₇₀ dyad was lower than that of the OPV-NDI dyad in solution. This result suggests that the intramolecular charge transfer from OPV to the acceptor was more efficient in the OPV-C₇₀ dyad than in the OPV-NDI dyad in CHCl₃. The thin film fluorescence spectra of the OPV-NDI dyad, OPV, and OPV-C₇₀ dyad are shown in Figure 2b. The films had a similar absorbance of approximately 0.5 at the excitation wavelength of 420 nm and the fluorescence intensity was normalized by the absorbance. The peak shifted from 485 nm in solution to 530 nm in the OPV pristine film. The fluorescence intensity of the OPV-NDI dyad was lower than that of OPV for the thin film spectra, demonstrating that excited state of the OPV moiety was quenched by NDI in the OPV-NDI dyad thin film. The OPV-C₇₀ dyad showed a lower fluorescence intensity than the OPV-NDI dyad for the thin film spectra, similar to the solution spectra, indicating that C₇₀ fullerene quenched the fluorescence of OPV more efficiently than did NDI.

Cyclic voltammetry

The half potentials of first oxidation (E_{ox}) and the reduction (E_{red}) of CHCl₃ solutions of the OPV-NDI dyad, OPV, and NDICOOH relative to the redox potential of Fc/Fc⁺ were determined by CV (see Supporting Information for the voltammogram). The energy levels of the HOMO and LUMO were estimated by assuming the Fc/Fc⁺ redox potential to be -4.8 eV relative to the vacuum level.²⁸ E_{ox} and E_{red} of the OPV-NDI dyad were 0.36 and -1.09 V, respectively, and E_{ox} of OPV and E_{red} of NDICOOH were 0.37 and -1.05 V, respectively. E_{ox} of NDICOOH and E_{red} of OPV were not observed. The OPV-NDI dyad had an E_{ox} and E_{red} similar to those of OPV and NDI, respectively. This indicates that the oxidation of the OPV moiety and the reduction of the NDI moiety in the OPV-NDI dyad were not affected by the covalent attachment. The LUMO energy offsets between the OPV and NDI moieties in the dyad, calculated from E_{ox} and the optical band gaps of the OPV moiety and E_{red} of the NDI moiety, were around 1.1 eV, which is much higher than the energy required for efficient charge separation in

Thermal properties

DSC of the OPV-NDI dyad, OPV, and NDICOOH was conducted with a scan rate of 10 °C min⁻¹, and the results of the second scans are shown in Figure 3. OPV exhibited an endothermic peak at 194 °C upon heating, and an exothermic peak at 176 °C upon cooling. NDICOOH showed an endothermic peak at 210 °C upon heating, and an exothermic peak at 175 °C upon cooling. In contrast, the OPV-NDI dyad showed two endothermic peaks at 148 and 172 °C upon heating, and two exothermic peaks at 146 and 122 °C upon cooling. This result suggests that there was a mesophase in the OPV-NDI dyad in the temperature range of 148-172 °C upon heating and 122-146 °C upon cooling caused by the partial melting of one of the components. The structural change at high temperatures is discussed in the following section. The OPV-C₇₀ dyad showed one endothermic peak at 187 °C and one exothermic peak at 154 °C, as previously reported.¹⁸

3.3. Crystal structure

2D-GIXRD of thin films

2D-GIXRD patterns were measured for the spin-coated OPV, NDICOOH, OPV-NDI dyad, and OPV-C₇₀ dyad films on silicon substrates. The thin films were prepared by spin coating CHCl₃ solutions with a total concentration of 10 mg mL⁻¹ at 2500 rpm. The samples were not thermally annealed. Figure 4b, shows that the NDICOOH pattern contained several diffraction peaks in the out-of-plane and in-plane directions. The strongest peak at $q_z = 0.34 \text{ \AA}^{-1}$ in the out-of-plane direction represented a d -spacing of 1.9 nm. The integrated linear profiles are shown in the Supporting Information. NDI-based molecules tend to have lamellar structures in spin-coated films,³⁰ and the pattern suggested the preferential orientation of the lamellar structure perpendicular to the substrate. The packing lattice spacing from the diffraction peak was close to the calculated molecular length along the long axis of NDICOOH (2.2 nm).

The shorter packing length **implies** that the molecular packing axis could be slightly tilted.³¹ The OPV film showed diffraction peaks at $q_z = 1.40 \text{ \AA}^{-1}$ in the out-of-plane direction and $q_{xy} = 1.40, 1.67 \text{ \AA}^{-1}$ in the in-plane direction, with d -spacings of 0.45 and 0.38 nm, respectively, corresponding to the reported peaks of the herringbone structure.³²

The OPV-NDI dyad showed diffraction peaks in the z -direction at $q_z = 0.27 \text{ \AA}^{-1}$ (Figure 4c), which is similar to the diffraction pattern of NDICOOH. The strongest diffraction peak at $q_z = 0.27 \text{ \AA}^{-1}$ represented a d -spacing of 2.4 nm. Assuming that NDI has a lamellar structure in OPV-NDI films similar to that of NDICOOH, the packing lattice spacing may be longer than NDICOOH because of the hexaethylene glycol linker. The diffraction peak at $q_z = 1.41 \text{ \AA}^{-1}$ ($d = 0.44 \text{ nm}$) of the OPV-NDI film demonstrated the existence of an OPV herringbone structure in the dyad film. No other peaks that could be assigned to the D/A alternating structures were observed. In contrast, the 2D-GIXRD pattern for the OPV-C₇₀ dyad film (Figure 4d), contained no peaks from the OPV packing structure because the bulky C₇₀ disturbed the OPV packing. These results suggest that in the OPV-NDI dyad film, OPV and NDI aggregated and crystallized separately to form the structures similar to those in the pristine films. This difference probably arose because C₇₀ is globular and less crystalline whereas NDI is planar and highly crystalline. **To discuss morphology further, AFM image of the dyad film were measured (see Supporting information). The image shows the presence of grains with the size of ca. 100 nm reflecting the highly crystalline character of OPV-NDI dyad. It is difficult to observe microphase separation of the donor and the acceptor domains probably because it is too small, so the detailed information of morphology such as crystallite size or connectivity remains unknown. Further analysis on the crystallized domain sizes and the connectivity and how to control them in the films would be challenges for the future.**

Variable temperature XRD

Powder XRD patterns of OPV-NDI dyad were measured at 30, 160, and 190 °C upon heating, and 130 and 100 °C upon cooling (Figure 5). These temperatures corresponding to below and above the

phase transitions observed in the DSC measurements (Figure 3). Diffraction peaks from the long axis of NDI at 5.0°, and peaks from the OPV herringbone structure at 19.5, 21.0, and 23.6° were observed at 30 °C. At 160 °C, the NDI diffraction peak at 5.0° disappeared, although the OPV peaks at 19.5, 21.0, and 23.6° remained. At 190 °C, the OPV diffraction peaks also disappeared. The film was cooled to 130 °C and only the OPV peaks at 19.5, 21.0, and 23.6° appeared. Upon further cooling to 100 °C, the diffraction peaks from the NDI lamellar structure at 5.0° were observed. This indicates that the exothermic peaks at 148 and 172 °C during heating in the DSC measurements (Figure 3) correspond to the melting of NDI and OPV, and the endothermic peaks at 146 and 122 °C correspond to the recrystallization of OPV and NDI, respectively. The distinct temperature responses of OPV and NDI in the OPV-NDI dyad strongly suggest that the two moieties were packed separately in the solid state. This is consistent with the 2D-GIXRD results for the thin films. Although electron donating and accepting moieties could stack alternately because of a D/A interaction,³³⁻³⁵ the rod-like structure of OPV and the planar structure of NDI meant they formed separate ordered structures in the films.

3.4. Photovoltaic properties

OSC devices containing the OPV-NDI dyad as the active layer were fabricated. Thickness of the active layers of OPV-NDI dyad was 110 nm measured by surface profilometry. The *J-V* curves and EQE spectra of the devices without thermal annealing are shown in Figure 6. The device properties were: $J_{SC} = 0.31 \text{ mA cm}^{-2}$, $V_{OC} = 0.91 \text{ V}$, $FF = 0.28$, and $PCE = 0.08\%$. The EQE spectra in Figure 6b shows that the devices had a photocurrent response corresponding to the absorption of both the OPV moiety peaked at 440 nm and the NDI at 360 nm and 380 nm. Thermal annealing at temperatures up to 160 °C did not affect the device performance substantially (see Supporting Information).

Compared to the photovoltaic performance reported for the OPV-C₇₀ dyad ($J_{SC} = 4.6 \text{ mA cm}^{-2}$, $V_{OC} = 0.91$, $FF = 0.46$ and $PCE = 1.92\%$), the OPV-NDI dyad showed the same V_{OC} and a smaller photocurrent and FF , resulting in lower performance.¹⁸ Morphology, which largely affects charge

transfer, separation and transport in general, was drastically changed from OPV-C₇₀ dyad to OPV-NDI dyad, therefore it is difficult to consider the limiting factor of J_{SC} and FF in OPV-NDI dyad. One possible reason for the lower photocurrent in OPV-NDI is the lower efficiency of the photoexcited charge transfer from OPV to NDI, as suggested by the fluorescence measurements in Figure 2. There are few reports of highly efficient OSCs using non-functionalized NDI as an electron acceptor,²⁰ even though NDI has a high electron mobility.²⁴⁻²⁵ Recent report clarified that local molecular orientation at the D/A interface played a key role for charge generation in asymmetric acceptors alternative to fullerene acceptors.³⁶ Smaller electronic coupling between OPV and NDI in thin films might be the other possible reason for lower charge generation ability in OPV-NDI than in OPV-C₇₀ dyad. Although we observed the separated crystallization of the donor and acceptor in the film, the FF of the cell was quite low. This could be because of the molecular orientation; 2D-GIXRD denotes that the π - π stacking is oriented parallel to the substrate in the NDI phases, which is not suitable for charge conduction in the vertical direction. Control of the molecular orientation in the films could improve the transport.²⁷ Recently, non-fullerene small molecule acceptors have been explored,³⁷⁻³⁸ such as perylenediimides (PDI) derivatives,³⁹ vinazene derivatives,⁴⁰ and oligothiophene-functionalized NDI.²⁹ Sharenko et al. reported an OSC performance of 3.0% by using a PDI derivative.⁴¹ Substitution of NDI with another efficient planar acceptor, such as PDI, might produce a well-defined nanostructure and efficient OSC device performance.

4. Conclusions

In OPV-NDI dyad films, the OPV and NDI moieties aggregate and crystallize separately because of the different crystalline properties of the components. This suggests that separate donor and acceptor phases can be spontaneously constructed in the spin-coated films by using the dyad system with flat, crystalline molecules. This design for the dyad molecules could be used to achieve nanoscale ordering in organic electronics devices.

ACKNOWLEDGMENT: This research was supported by JST, PRESTO. GIXRD experiments were performed at BL19B2 at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal 2013A1634). The authors thank Dr. Itaru Osaka at RIKEN for help with GIXRD measurements. S.I. thanks JSPS for financial support.

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Scheme 1. Synthetic route to the OPV-NDI dyad.

Figure 1. Absorption spectra of (a) the OPV-NDI dyad (solid line), OPV (dashed line), and NDICOOH (dotted line) in CHCl_3 and (b) OPV-NDI dyad (solid line), OPV (dashed line), and OPV- C_{70} dyad (dash-dotted line) thin films.

Figure 2. Fluorescence spectra of (a) OPV-NDI dyad (solid line), OPV (dashed line), OPV-C₇₀ dyad (dash-dotted line), and mixture of OPV and NDICOOH (dotted line) in CHCl₃ and (b) OPV-NDI dyad (solid line), OPV (dashed line), and OPV-C₇₀ dyad (dash-dotted line) thin films.

Figure 3. DSC charts of OPV-NDI dyad (solid line), OPV (dashed line), and NDICOOH (dotted line). The profiles are shifted in the y-axis for clarity.

Figure 4. 2D-GIXRD patterns of (a) OPV, (b) NDICOOH, (c) OPV-NDI dyad, and (d) OPC-C₇₀ dyad thin films.

Figure 5. Powder XRD patterns of the OPV-NDI dyad at different temperatures. The patterns are shifted in the y-axis for clarity.

Figure 6. (a) J - V curves (dashed line: in the dark, solid line: under simulated solar light irradiation (AM 1.5)) and (b) EQE spectrum of the OSC devices containing the OPV-NDI dyad.

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