Miscibility-Controlled Phase Separation in Double-Cable Conjugated Polymers for Single-Component Organic Solar Cells with Efficiencies over 8%

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ABSTRACT

In this work, a record power conversion efficiency of 8.40% was obtained in single-component organic solar cells (SCOSCs) based on double-cable conjugated polymers. This is realized based on the finding that exciton separation plays the same important role as charge transport in SCOSCs. Herein, we designed two double-cable conjugated polymers with almost the identical conjugated backbones and electron-withdrawing side units, but the extra chlorine (Cl) atoms had different positions on the conjugated

backbones. We found that, when Cl atoms were positioned at the main chains, the polymer formed the twist backbones, enabling better miscibility with the naphthalene diimide side units. This could improve the interface contact between conjugated backbones and side units, resulting in efficient conversion of excitons into free charges. These observations were confirmed by systematical studies via several advanced measurements. These findings reveal the importance of charge generation process in SCOSCs and also suggest a strategy to improve this process, that is, controlling the miscibility between conjugated backbones and aromatic side units in double-cable conjugated polymers.

Keywords: single-component organic solar cells; double-cable conjugated polymers; naphthalene diimide; miscibility; phase separation.

1. INTRODUCTION

Organic solar cells (OSCs) can be classified into three types based on the number of conjugated materials in the photo-active layers, which are single-component,^[1] two-component^[2] and three-component solar cells.^[3] Nowadays, two and three-component OSCs that use physically blended electron donor and acceptor as photoactive layer, have been widely investigated and the power conversion efficiencies (PCEs) are now approaching 18%.^[4] In contrast, single-component OSCs (SCOSCs) have been somehow ignored by researchers in the past two decades, although they have exhibited superior stability that is a prerequisite for real applications.^[5] Single-component conjugated materials contain diblock conjugated polymers,^[6] double-cable conjugated polymers^[7] and molecular dyads,^[8] but most of them were limited to polythiophene derivatives. The widely developed “donor-acceptor” conjugated polymers^[9] and non-fullerene acceptors^[10] have been rarely incorporated into the single-component materials. Another drawback is the difficulty to obtain the optimized phase separation between donor and acceptor segments in a single material, resulting in severe charge recombination and low charge transport efficiency. As a consequence, SCOSCs showed the highest PCE of 6.3% that was far lagging behind two-component OSCs.^[7i]

We have been particularly interested in double-cable conjugated polymers for application in SCOSCs since they could be synthesized via a controllable manner, in which a series of functionalized monomers with pendent electron acceptors were prepared for palladium-catalyzed polymerization.^[11] This enabled us to incorporate the widely reported conjugated polymers and electron acceptors into double-cable polymers, providing tunable optical and electrical properties.^[7h-m, 12] Among them, we found that the linear conjugated backbones^[7h] and post-thermal treatment^[7i] could facilitate the simultaneous self-assembly of conjugated backbones and aromatic side units, generated well-ordered nanophase separation, and hence provided external quantum efficiencies (EQEs) above 0.65 and PCEs over 6%. These results still leave two questions to be answered: (1) why are the EQEs of SCOSCs still below those (over 0.80) of two-component OSCs even though these double-cable polymers have ordered nanostructures and (2) what are the intrinsic parameters that control the phase separation in double-cable polymers?

Double-cable conjugated polymers are principally a kind of graft polymers, so that they follow the similar rules for phase separation.^[13] It have been reported that miscibility played an important role in the phase separation of graft polymers^[14] as well as diblock copolymers.^[15] Miscibility was further used to study the phase separation of two mixed conjugated materials in two-component OSCs.^[16] In general, a mixed two-component system contains pure donor, pure acceptor, and mixed phases. Miscible donor and acceptor enabled the formation of well-mixed phase, which could enhance the donor/acceptor interface area and hence improved the exciton separation efficiency.^[17] We envision that the mixed phase in double-cable polymers that creates the interface between donor and acceptor segments is also critically important for exciton separation. However, this process has been usually ignored since most studies in SCOSCs focused on the charge transport process.

In this work, we elucidate the important role of miscibility on the phase behavior of double-cable polymers and its consequence on the photoelectric conversion process in SCOSCs. This was realized by designing two double-cable polymers JP01 and JP02 (**Figure 1a** and **b**) with similar conjugated backbones and naphthalene diimides (NDIs)

as side units, while the position of chlorine (Cl) atoms at the backbones is different. Differential scanning calorimetry (DSC) and contact angle measurements indicated that conjugated backbones and NDI side units in JP02 showed good miscibility compared to JP01, resulting in efficient exciton separation. Therefore, a PCE of 8.4% that represented the record PCE in SCOSCs was obtained, together with EQEs over 0.75 and fill factors (FFs) close to 0.70. These results demonstrate that in SCOSCs exciton separation process has the same role with charge transport process, and miscibility between donor and acceptor segments in double-cable polymers is the critical factor to control this process.

Figure 1. The chemical structures of the double-cable conjugated polymers (a) JP01 and (b) JP02, and the donor polymers (c) PBDB-T-Cl, (d) PCIBDB-T and (e) the acceptor NDI. EH is 2-ethylhexyl.

2. RESULTS AND DISCUSSION

2.1. Design motif of using NDI side units

This is the first time to use NDI side units in double-cable polymers. In previous studies, these polymers always contained fullerene derivatives or perylene bisimides (PBIs) as side units since their large π conjugated units enabled the double-cable polymers to form ordered nanostructures, but meanwhile these polymers performed

limited solubility. When using the small NDIs as pendent groups, surprisingly, the new polymers JP01 and JP02 showed good solubility in nonhalogenated solvents, such as toluene and even tetrahydrofuran (THF) (**Figure S1**). In contrast, the donor polymers PBDB-T-Cl, PCIBDB-T (**Figure 1c** and **d**) and the PBI – based double-cable polymer PBDBPBI-Cl^[7i] (**Figure S1a**) were insoluble in these solvents (**Figure S1**). Combining with the record PCEs of SCOSCs based on JP02, the NDI – based double-cable polymers are the promising candidates toward high performance and environment-friendly SCOSCs.

2.2. Synthesis and characterization

JP01 and JP02 were prepared as similar to previous procedures (**Scheme S1**).^[7i] It is worth mentioning that the monomer **M1** with pendent NDIs was prepared in a high yield (84%) compared with the monomer with pendent PBIs (yield: 44%),^[7i] which is also one of the merits for NDI – based double-cable polymers. JP01 and JP02 showed the number-average molecular weight (M_n) of 68.3 kDa and 37.9 kDa, as determined by gel permeation chromatography (GPC) with *o*-DCB as the eluent at 140 °C (**Table S1**). They also exhibit high thermal stability up to 400 °C (**Figure S2a**). We could also obtain a relatively low molecular weight JP01 with $M_n \sim 40$ kDa when using a short polymerization time (12 h), which is comparable with M_n of JP02. Since we found that this low molecular weight JP01 could also exhibit similar PCEs as the high molecular weight one, we intended to use JP01 with M_n of 68.3 kDa for the following studies.

JP01 and JP02 show similar absorption spectra in the solution and thin films, in which two absorption bands can be observed: one band at 300 – 400 nm is attributed to the absorption from NDIs, and another band at 500 – 700 nm is originated from the conjugated backbones (**Figure S2b** and **Figure 2a**). The absorption peaks at the region of 500 – 700 nm for JP01 and JP02 are red-shifted over 10 nm compared to those of donor polymers PBDB-T-Cl and PCIBDB-T (**Table S2**), indicating that the conjugated backbones in JP01 and JP02 gain better aggregation/crystallization in thin films. This unusual phenomenon is absent in the PBI – based polymer PBDBPBI-Cl.^[7i] It is also interesting to mention that, PCIBDB-T exhibited red-shift absorption spectra compared

to that of PBDB-T-Cl, which should be due to the electronegative effect of Cl atoms.^[18] The frontier energy levels of JP01 and JP02 were determined by cyclic voltammetry (CV) measurements, as shown in **Figure S3** and **Figure 2b**. Both of JP01 and JP02 have the similar lowest unoccupied molecular orbital (LUMO) levels with that of the NDI acceptors, while their highest occupied molecular orbital (HOMO) levels are slightly deeper than those of donor polymers (**Figure 2b**). From the red-shifted absorption spectra and high-lying HOMO levels, it seems that NDIs are helpful for the crystallization of conjugated backbones.

Figure 2. (a) Optical absorption spectra of thin films and (b) HOMO/LUMO energy levels determined from CV measurement vs. Fc/Fc^+ based on the polymers and **NDI** thin films. DSC heating and cooling traces (second cycle) of (c) JP01, JP02 and (d) the acceptor **NDI** at a scanning rate of 10 °C/min under N_2 (exo. up).

2.3. Amorphous region studied by miscibility analysis

We firstly analyze the mixing behavior between donor and acceptor segments in the amorphous region via the Flory-Huggins interaction parameter (χ), which was studied by differential scanning calorimetry (DSC) and contact angle in this work.

There is no thermal transition in the donor polymers PBDB-T-Cl and PCIBDB-T (**Figure S2c**). The electron acceptor **NDI** exhibits two sharp peaks during heating and cooling process with high enthalpies over 80 J/g (**Figure 2d**), corresponding to melting and crystallization. When NDI was incorporated into the double-cable polymers, the melting temperature and enthalpy were decreased (**Figure 2c**) regardless of the positions of Cl atoms. Importantly, JP02 shows lower melting temperature (150.1 °C) and enthalpy (5.59 J/g) than those in JP01, indicating that in JP02 the conjugated backbones and NDIs have better miscibility. This can be further quantified with χ obtained from DSC melting point depression analysis.^[17] The details of this analysis are listed in the Supplementary Information. We found that JP01 had a much higher χ (1.02) compared to JP02 ($\chi = 0.57$).

We can also qualitatively compare the miscibility via calculating χ between the donor polymers PBDB-T-Cl, PCIBDB-T and the acceptor **NDI** from contact angle measurement, as shown in **Figure S4** and **Table 1**. The surface energy and solubility parameter of PCIBDB-T are close to the acceptor **NDI**, and hence their χ is $0.14k$ (k is a constant as denoted in **Table 1**). This is much lower than that between PBDB-T-Cl and NDI with χ of $1.19k$. This observation is consistent with the results from DSC measurements.

It is interesting to discuss the origin of different miscibility between conjugated backbones and NDIs in JP01 and JP02. Although they contain the same atoms, the position of Cl can influence the conformation of conjugated backbones. In JP02, Cl atoms cause the twisted backbones with the dihedral angle of 19.4°, while it is decreased to 1.3° in JP01 (**Figure S5**). We speculate that, the twisted backbones in JP02 can hamper the crystallization of conjugated backbones in the amorphous regions, so that NDIs can penetrate into the conjugated backbones and create more donor/acceptor interface for exciton separation.

Table 1. The surface energy and solubility parameter of the donor polymers and **NDI**, and the Flory-Huggins interaction parameter (χ).

<i>materials</i>	<i>surface energy</i>	<i>solubility parameter</i>	χ_{ij}^c
	γ (mN/m) ^a	δ (MPa ^{1/2}) ^b	
PBDB-T-Cl	21.58	17.04	1.19 κ^d
PCIBDB-T	18.02	15.57	0.14 κ^e
NDI	18.91	15.95	-

^a The calculation for γ is present in Equation S1 in the Supporting Information. ^b $\delta = K\sqrt{\gamma}$, where K is the Proportionality constant ($K = 116 \times 10^{-3} \text{ m}^{-1/2}$).^[19] ^c $\chi_{ij} = k(\delta_i - \delta_j)^2$, where k stands for V_0/RT . Herein i and j denote the donor and acceptor segments, respectively. V_0 is the geometric mean of the polymer segment molar volume, R is the gas constant, T is the absolute temperature. ^d Interaction between PBDB-T-Cl and **NDI**. ^e Interaction between PCIBDB-T and **NDI**.

2.4. Crystalline region studied by XRD

We then study the crystalline regions of JP01 and JP02 films by two-dimensional X-ray diffraction techniques (including wide-angle and medium-angle, GIWAXS and GIMAXS), as shown in **Figure 2** and **Table 2**. Summary of GIWAXS peak fitting results were present in **Figure S6-S7**. Both JP01 and JP02 exhibit temperature – driven phase separation as evidenced by the preferential face-on orientation (**Figure 2a**) and enhanced coherence lengths (CLs) (**Table 2**) after thermal treatment on the polymer films. This can also be observed in the PBI – based double-cable polymer.^[7i] In addition, the polymer films annealed at high temperature present fine diffraction peaks, as shown both in the GIWAXS and GIMAXS patterns (**Figure 3a** and **c**). Among them, the diffraction peak q_1 located at $0.15 \text{ \AA}^{-1}$ with a d -spacing of 4.2 nm is corresponding to the lamellar stacking of conjugated backbones (**Figure 4a**). This distance is lower than that in PBDBPBI-Cl films (6.9 nm) due to the small NDI compared to PBI.^[7i] The diffraction peak q_2 with a d -spacing of 2.0 nm should be assigned to the second order peak of q_1 , but the intensity of the peak q_2 is obviously high compared to the peak q_1 , which would be the overlap of the peak $q_{(001)}$ as the repeat units of conjugated

backbones (**Figure 4a**).^[71] New peaks located at $0.72 \text{ \AA}^{-1}$ can also be observed after thermal treatment of the JP01/JP02 films, but currently we are unable to assign these peaks. Further analysis of the size of crystal domains in these thermal-annealed polymer thin films by coherence lengths (CLs) reveals that, JP01 and JP02 show quite similar CLs for q_1 , q_2/q_{001} and q_{010} peaks, indicating that they have the similar degree of crystallization in the crystalline region (**Table 2**).

Figure 3. Characteristics of the polymer thin films spin-casted on Si substrates without or with annealing. (a) GIWAXS patterns, (b) the OOP and IP cuts of the corresponding GIWAXS patterns, and (c) GIMAXS patterns. JP01 thin films were fabricated from toluene and JP02 thin films were fabricated from toluene/DIO (2%) solution, which was consistent with the optimized SCOSCs.

Table 2. Crystallographic parameters of the polymer JP01 and JP02 in thin films.

polymer	Temp	q_1			q_2+q_{001}			q_{010}		
		q ($\text{\AA}^{-1}$)	d (nm)	CL (nm)	q ($\text{\AA}^{-1}$)	d (nm)	CL (nm)	q ($\text{\AA}^{-1}$)	d ($\text{\AA}$)	CL (nm)
JP01 ^a	RT	0.15	4.2	7.89	0.31	2.1	8.05	1.71	3.67	1.77
	200 °C	0.15	4.2	16.2	0.31	2.0	12.3	1.72	3.64	2.24
JP02 ^b	RT	0.15	4.2	9.85	0.31	2.1	9.20	1.72	3.66	1.96
	150 °C	0.15	4.2	15.7	0.31	2.0	12.2	1.73	3.64	2.26

^a JP01 thin films were fabricated from toluene solution. ^b JP02 thin films were fabricated from toluene/DIO (2%) solution.

From the analyses above, we intend to conclude that, JP01 and JP02 have similar crystallinity in the crystal region but different aggregation tendency in the amorphous phase. The crystalline region is helpful for charge transport, while the amorphous region is essential for exciton separation, as shown in **Figure 4b**. In JP02, conjugated backbones and NDIs have better miscibility, so as to create more interface to facilitate the exciton separation. In the following section, we will discuss the effect of the distinct phase separation on the photovoltaic performance, and study the charge generation and transport in detail.

Figure 4. (a) The ideally model to illustrate the crystalline region in JP01 film. (b) The simple scheme represents the crystalline and amorphous regions of double-cable polymers and the path for exciton separation and charge transport.

2.5. SCOSCs

JP01 and JP02 were then applied as the single photoactive layer for SCOSCs by using an inverted configuration with ITO/ZnO and MoO₃/Ag as the electrodes. The photoactive layers were spin-cast from the polymer solutions in toluene or THF, in which the high boiling point additive 1,8-diiodooctane (DIO), thermal-annealing temperature and the thickness were carefully optimized (**Table S3-S8**). The *J-V* characteristics from the optimized solar cells are shown in **Figure 5** and the photovoltaic parameters are summarized at **Table 3**. We also fabricated JP01 and JP02 thin films by using chlorobenzene without or with DIO as additive, and the corresponding SCOSCs exhibited relatively low PCEs (4.71% for JP01 and 7.08% for JP02, **Table S3** and **S6**). Interestingly, JP01-based cells exhibited optimized PCEs when the JP01 thin films were fabricated from toluene without DIO as additive (**Table S3**),

while JP02 thin films required DIO as additive to improve the PCEs (**Table S6**). From atomic force microscopy measurement, it clearly showed that the optimized JP01 and JP02 thin films had relatively low roughness with small domain size (**Figure S8b** and **Figure S9b**), indicating that better nanophase separation between backbones and NDIs could be obtained. Similar phenomenon could also be observed in our previous study, in which good crystalline cooperativity was linked to good nanophase separation.^[7k] Further studies by GIWAXS revealed that these optimized thin films had relatively high CLs of q_2/q_{001} and q_{010} peaks, corresponding to the better molecular packings (**Figure S10** and **Table S9**).

Figure 5. Characteristics of JP01 and JP02 based SCOSCs. **(a)** *J*-*V* characteristics in dark (dashed line) and under white light illumination (solid line). **(b)** EQE of the optimized SCOSCs. **(c)** Fraction of photons absorbed in the photoactive layers. **(d)** Calculated IQE spectra of SCOSCs. The thickness of JP01 and JP02 thin films for all these characteristics is 70 nm.

Table 3. Characteristics of optimized SCOSCs based on JP01 and JP02 fabricated from

different solvent.

Active layer	solvent	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE ^c (%)
JP01 ^a	Toluene	8.20 (8.47±0.18)	1.00 (0.98±0.01)	0.62 (0.60±0.02)	5.06 (4.90±0.12)
	THF	7.61 (7.19±0.66)	0.99 (0.98±0.01)	0.60 (0.65±0.06)	4.56 (4.53±0.05)
JP02 ^b	Toluene/DIO (2%)	12.81 (12.84±0.09)	0.94 (0.95±0.01)	0.69 (0.67±0.01)	8.40 (8.21±0.13)
	THF	12.0 (11.78±0.20)	0.92 (0.93±0.01)	0.65 (0.64±0.01)	7.18 (7.0±0.15)

^a The active layers were annealed at 200 °C for 10 min. ^c The active layers were annealed at 150 °C for 10 min. ^c Average PCEs are obtained from 6 devices.

JP01 – based SCOSCs exhibited a PCE of 5.06% with a short-circuit current density (J_{sc}) of 8.20 mA/cm², an open-circuit voltage (V_{oc}) of 1.00 V and FF of 0.62, while the PCE of SCOSCs based on JP02 was boosted to 8.40% with significantly enhanced J_{sc} of 12.81 mA/cm² and FF of 0.69. V_{oc} of the JP02-based solar cell was reduced to 0.94 V. Both of JP01 and JP02 based SCOSCs provided much higher PCEs than those of PBDB-T-Cl:**NDI** and PCIBDB-T:**NDI** based two-component solar cells (with PCEs of 0.65% and 1.09%, **Table S10-11**), exhibiting the superior advantage of SCOSCs. The improved J_{sc} in the JP02 based cell was reflected by its high external quantum efficiency (EQE) (**Figure 5b**). SCOSCs based on JP02 had high EQEs up to 0.75, while the EQEs in JP01 based solar cells were below 0.56. The J_{sc} s integrated from EQE spectra were 7.85 mA/cm² and 11.67 mA/cm², which agree within 10% of the measured J_{sc} s from AM1.5G solar simulator.

We further determined the fraction of absorbed photons (**Figure 5c**) and the internal quantum efficiencies (IQEs) of the solar cells (**Figure 5d**) from transfer matrix simulations.^[20] The absorption of polymer thin films in different thicknesses, and the

corresponding refractive index (n) and extinction coefficient (k) were summarized in **Figure S11**, which could be used to calculate the fraction of absorbed photons by JP01 and JP02 thin films in real devices. Interestingly, the absorption in the same thickness, extinction coefficient and the fraction of absorbed photons are all expected to be higher in JP02, than those in the JP01 film with the thickness of 70 nm, which is one reason for the higher J_{sc} in JP02-based solar cells. In addition, we found that JP02 based cells showed IQEs over 0.80, noticeably higher than the IQEs of the JP01 based solar cells. This further contributes to the higher J_{sc} in the solar cells based on JP02.

The photoactive layers fabricated from THF solution also exhibit descent PCEs in SCOSCs with 4.56% based on JP01 and 7.18% based on JP02 (**Table 3**). We also provided the stability test of these SCOSCs, in which JP01-based cells exhibited almost 100% of initial PCEs and JP02-based cells showed ~94% of initial PCEs after 150 h (**Figure S12**), exhibiting their good stability as also observed in our previous studies.^[5a]

2.5. Study of exciton separation in SCOSCs

Compared to the solar cell based on JP01, the increased IQE of the solar cells based on JP02 are expected to be a result of an improved charge generation efficiency, which is related to the degree of phase separation and energetics at the interface between the donor and acceptor segments. Firstly, we used steady-state photoluminescence (PL) to study the quenching efficiencies in JP01 and JP02 (**Figure 6a**). Both the donor polymers PBDB-T-Cl and PCIBDB-T exhibited strong PL emissions in the wavelength range of 600 – 1000 nm. In JP02 with NDI side units, donor emission is significantly quenched with quenching efficiency over 95%. However, in JP01, we find that quenching efficiency is as low as $\approx 40\%$, suggesting a poor generation of charge carriers. These significant PL differences reveal that JP01 has phase separated structures while JP02 shows mixed phase, which is consistent with miscibility studies.

The reason for the poor quenching efficiency in JP01 could be possibly due to insufficient energy offset between the CT states and the locally excited states of the conjugated backbones, preventing excitons to dissociate into CT states and free charge carriers. Therefore, we further characterized the charge transfer states (CTs) in these

solar cells, using the electroluminescence (EL) (**Figure 6b**) and sensitive EQE (sEQE) measurement (**Figure 6d-e**). In order to exactly obtain the optical band gap (E_g) of the polymers, we use the intersection of the absorption and PL spectra to define the E_g , as 1.87 eV for JP01 and 1.85 eV for JP02 (**Figure 6c**). The energy of CT (E_{CT}) of the solar cells based on JP01 and JP02 are determined by fitting to the low energy part of the sEQE spectra using the Marcus Theory.^[21] We found that E_{CT} of the solar cell based on JP01 was 1.65 eV, much higher than that of the JP02-based cell (1.55 eV) (**Table 4**). However, even for the solar cell based on JP01 with a larger E_{CT} of 1.65 eV, the energetic offset is expected to be over 0.2 eV, which should be enough for exciton dissociation.^[22] Thus, compared to the JP02 based solar cell, the poorer PL quenching efficiency, leading to lower J_{sc} in the solar cell based on JP01, is unlikely a result of insufficient energetic offset, and the phase-separated backbones and NDIs in JP01 should be the main reason for the low quenching ratio in PL spectra, resulting in low charge generation efficiency for JP01 – based SCOSCs.

The higher E_{CT} of the solar cell based on JP01, gives rise to a higher V_{oc} , compared to JP02. However, non-radiative voltage losses, determined by measuring the electroluminescence EQE (EQE_{EL}, **Figure 6f**) of the solar cells, were found identical for the solar cells based on JP01 and JP02, as summarized in **Table 4**. Note that the non-radiative voltage losses ($\Delta V_{oc}^{non-rad}$) of the SCOSCs based on JP01 and JP02 is now comparable to that of two-component solar cells, and much smaller than those in the previously reported SCOSCs.^[7i]

Figure 6. (a) Steady-state PL spectra of JP01 and JP02 films excited at 500 nm. (b) Normalized EL spectra of JP01 and JP02 based SCOSC devices, measured with an injection current of 1 mA. (c) Absorption and PL spectra for the calculation of optical band gap (E_g). (d-e) sEQE and EL spectra of JP01 and JP02 based SCOSCs devices, and fitting curves for the determination of E_{CT} . (f) EQE_{EL} of the SCOSCs.

Table 4. Characteristics of voltage loss in SCOSCs based JP01 and JP02.

polymer	E_g	qV_{oc}	E_{CT}	$q\Delta V_{oc}^{non-rad}$	E_{loss}
JP01	1.87	1.0	1.65	0.32	0.87
JP02	1.85	0.94	1.55	0.32	0.90

All values are in eV.

2.6. Study of excited state dynamics in SCOSCs

We then discuss the excited state dynamics by broadband transient absorption (TA) spectroscopy across a wide dynamic range from femto- to microseconds and broad spectral range (2.3 eV- 0.8 eV).^[23] **Figures 7a and 7c** show picosecond-nanosecond (ps-ns) TA spectra of JP01 and JP02 films excited at 650 nm. The negative $\Delta T/T$ signals represent photo-induced absorption (PIA), while positive $\Delta T/T$ signals represent the materials' photo-bleach (PB). The TA spectra at 500-700 fs (black line) showed a band centered at 1.1 eV, which we assigned to singlet exciton-induced absorption based on a

comparison with TA spectra of neat films (**Figure S13**). The singlet excitons exhibited a fluence independent decay within the first ~ 10 ps (**Figure S14**). During this time a new band emerges at 1.85 eV, which showed a fluence dependent rise, as is typical for charges.^[24] The charge generation kinetics of JP01 exhibit a slower rise (~ 30 ps at $4.2 \mu\text{J}/\text{cm}^2$) compared to that of JP02 (~ 15 ps at $4.2 \mu\text{J}/\text{cm}^2$). This indicates that more donor-acceptor interface is present, which facilitates charge generation in JP02. The decay dynamics of the generated charge carriers show a slower decay for JP02 compared to that of JP01. For instance, at a pump fluence of $4.2 \mu\text{J}/\text{cm}^2$ about 45% of the charges have decayed within 7 ns in JP01 (**Figure 7b**), while only 25% of the charges have decayed within 7 ns in JP02 (**Figure 7d**). This indicates slower charge recombination in JP02 and in turn implies that more charge carriers are available for extraction, well in line with the higher device performance.

Having revealed the exciton dissociation and charge generation dynamics, we turn to discuss the charge carrier recombination dynamics on a longer timescale. We used ns- μs TA spectroscopy to probe the charge carrier dynamics. On this time scale, all singlets have decayed and only charge carriers are left. **Figure 7e and f** show the charge carrier decay dynamics at various fluences. We quantified the non-geminate and geminate recombination rates and extracted the non-geminate recombination coefficient by using a two-pool model, previously introduced by Howard et al., and thereafter also applied to several other polymer:fullerene blends.^[25] Details of this model can be found elsewhere.^[25a] Here, we assumed the charge carrier cross-section as $1 \times 10^{-16} \text{ cm}^2$, a magnitude typically found in conjugated materials. We obtained the rate of charge transfer state to ground state recombination ($k_{CT \rightarrow GS} = 4.2 \times 10^8 \text{ s}^{-1}$, **Figure 7e**), larger than that of JP02 ($k_{CT \rightarrow GS} = 2.1 \times 10^8 \text{ s}^{-1}$, **Figure 7f**). The fit shows that both material systems exhibit very similar fractions of free charge carrier generation, yet their recombination differs. JP01 shows a larger bimolecular recombination coefficient ($4.64 \times 10^{-12} \text{ cm}^3/\text{s}$) compared to JP02 ($1.65 \times 10^{-12} \text{ cm}^3/\text{s}$). **Figure 7g** compares the decay dynamics at a fluence of $3.8 \mu\text{J}/\text{cm}^2$ of both thin films and clearly shows a slower decay in JP02. The slower recombination rate indicates longer charge carrier lifetime in JP02 blends. This is confirmed by transient

photovoltage (TPV) measurements, which showed that JP02 had a slightly longer charge carrier lifetime than JP01 (**Figure 7h**).

Figure 7. Picosecond-nanosecond TA spectra of (a) JP01 and (c) JP02 films respectively. Picosecond-nanosecond TA kinetics of selected PA region as indicated in the legend of (b) JP01 films and of (d) JP02 films. (e) The nanosecond-millisecond (ns-ms) TA kinetics of the entire PA region of JP01 and (f) JP02 for a wide range of fluences. The solid lines represent the two-pool model fit. (g) Comparison of ns-ms TA kinetics of both JP01 (black) and JP02 (red) at 3.8 μJ/cm². We note that the region around 1.5-1.6 eV is affected by the scattering of the pump (800 nm) used for generating the white light continuum. (h) Charge-carrier lifetime of the solar cells based on JP01 and JP02, determined by TPV decay measurement.

2.7. Charge transport studies by OFETs and SCLC

Charge transport properties can be studied by mobilities, as shown in **Figure 8** via organic field-effect transistors (OFETs) and space charge limited current (SCLC) measurement. From OFET devices, JP01 performed a hole mobility (μ_h) of $5.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and JP02 had a slightly low μ_h of $3.1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, we failed to extract electron mobilities from OFET devices (**Figure S15**). We speculate that NDIs in these double-cable polymers cannot generate the transport channels in the microscale (compared to the nanoscale transport in OSCs) that are used for electron transport from source to drain electrodes. We then used SCLC to determine the charge carrier

mobilities, in which JP01 and JP02 exhibited the μ_{hs} of $1.0 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $2.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (**Figure 8c**). Meanwhile, the electron mobilities (μ_{es}) of JP01 and JP02 extracted from SCLC measurements were $2.3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $5.9 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (**Figure S15c**). This indicated that, the ratio of μ_{h} and μ_{e} is 4.6 for JP02-based device, which is much lower than that for JP01-based device (as 43.5). The balanced hole and electron mobilities in JP02-based device would reduce the charge recombination, which is consistent with its high J_{sc} and FF in SCOSCs.

Figure 8. (a, b) Hole mobility extracted from transfer curves obtained from OFET devices, and (c) hole mobility extracted from SCLC measurement with hole-only devices based on JP01 and JP02 films with the thickness of 150 nm and 110 nm, respectively.

2.8. Discussion

We then provide some discussion about the origination of distinct photovoltaic performance based on JP01 and JP02. TA and TPV measurements revealed that JP02 had slightly less charge recombination, and SCLC measurements showed that JP02-based cells performed balanced hole and electron transport. These two factors enable better charge transport in JP02-based cells, explaining higher FFs (0.62 vs. 0.69 for JP01 and JP02 in **Table 3**). The better charge transport in JP02-based cells seems to be inconsistent with the observation that, JP01 and JP02 thin films have similar degree of crystallinity in the crystalline region. We think that charge transport in thin films is

simultaneously determined by crystalline and amorphous region, in which the aggregation of donor and acceptor segments in amorphous region would significantly contribute to the charge transport and recombination process.^[26] In another aspect, we have used DSC and contact angle measurement to clearly show the better miscibility in JP02, resulting in large interface area as also confirmed by PL and TA measurements. This directly linked to the efficient exciton separation efficiency, explaining the significantly enhanced J_{sc} s and PCEs in JP02-based SCOSCs.

Although we realized a record PCE for SCOSCs in this work, it is still far behind the performance of two-component OSCs. The EQEs and FFs in this work are still low but E_{loss} is high (**Table 4**) compared to those in two-component OSCs (usually EQEs over 0.80, FF over 0.75 and E_{loss} below 0.60 eV could be obtained). The new material design, concerning how to balance the miscibility and carrier mobilities, and how to reduce the E_{loss} , would enhance the PCEs of SCOSCs to over 10%. However, further enhancement of PCEs in SCOSCs requires the introduction of new electron acceptors, especially fused-ring acceptors with absorption in the near-infrared region to fully utilize the sunlight.^[27]

3. CONCLUSION

In this work, we designed and synthesized two new double-cable conjugated polymers for application in SCOSCs, in which a record PCE of 8.4% was obtained. We for the first time introduced NDI side units into double-cable polymers, and changed the position of Cl atoms to adjust the miscibility between conjugated backbones and side units. We found that, when Cl atoms were positioned at the main chains, the miscibility of the segments in JP02 was improved, which was helpful for the exciton diffusion and separation into free charges as confirmed by PL and TA measurements. As a consequence, JP02 – based SCOSCs provided a record PCE of 8.40%, as well as high EQEs over 0.75 and FFs close to 0.70. Moreover, we found that NDI contained double-cable polymers showed excellent solubility in non-halogenated solvents, such as toluene and THF. Therefore, NDI – based double-cable polymers have great potential application in high performance and environment - friendly SCOSCs.

Author Contributions

▽X. J., J. Y. and S. K. contributed equally to this work.

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Entry for the Table of Contents

Full Paper

A naphthalene diimide based double-cable conjugated polymer provided a record efficiency of 8.4% in single-component organic solar cells when simultaneously facilitating exciton separation and charge transport via miscibility control.

Xudong Jiang, Jinjin Yang, Safakath Karuthedath, Junyu Li, Wenbin Lai, Cheng Li, Chengyi Xiao, Long Ye, Zaifei Ma, Zheng Tang, Frédéric Laquai, Weiwei Li*

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Miscibility-Controlled Phase Separation in Double-Cable Conjugated Polymers for Single-Component Organic Solar Cells with Efficiencies over 8%