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Supporting Information

N-doping semiconductive polymer by methoxy-modified JLBI towards optimized miscibility and Coulomb interactions for high thermoelectric performance

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1. Materials

Chemicals are obtained from Sinopharm Chemical reagents and Energy Chemistry and are used as received unless otherwise stated. N2200 (Mn = 4.4×10^4 , PDI = 2.02) was purchased from SunaTech Inc. 8-hydroxyjulolidine-9-carboxaldehyde was purchased from Energy Chemicals. *N*, *N*'-dimethyl-o-phenylenediamine (N-DMBI) was purchased from Sigma-Aldrich. The 9-(1, 3-dimethyl-2, 3-dihydro-1hbenzimidazole-2-yl)-julolidine (JLBI) were synthesized as previously reported.¹

2. Measurements and Instruments

¹H NMR and ¹³C NMR spectra were performed on a Bruker Advance III-HD-500MHz at 298K in CDCl₃ with tetramethylsilane (TMS) as the internal standard. The chemical shifts (δ) are reported in parts per million (ppm). NMR spectra for **MeO-JLBI** are shown in Fig S4. and S5. The mass spectroscopy measurement (Fig. S6) was performed on a SHIMADZU GCMS-QP2020 spectrometer.

Thermogravimetric analysis (TGA) was conducted on a NETZSCH-STA449C from 30 to 500 °C under N₂ at a heating rate of 10 °C min⁻¹. Differential scanning calorimetry (DSC) measurement of the pristine dopant was carried out from 30 to 200 °C under N₂ at a heating rate of 10 °C min⁻¹ on a PerkinElmer DSC-8500 instrument. The samples were vacuum oven-dried overnight before TGA and DSC measurements. Cyclic voltammetry (CV) experiments on MeO-JLBI were conducted in a CHI 605E analyzer at room temperature. The measurements were performed in 0.1 M Bu₄NPF₆ in deaerated anhydrous acetonitrile using a conventional three-electrode setup: a platinum

wire counter electrode, a platinum disk working electrode, and ferrocene as the internal reference, at a scan rate of 0.1 V s^{-1} .

All calculations of electronic structures and energy were carried out with the Gaussian 16 software. To simplify the calculations, we replace the alkyl side chain of N2200 with a methyl group.² The geometry optimization was carried out using the B3LYP functional, $6-31G^*$ basis set, combined with the DFT-D3 correction level. The single-point energy calculation was performed using the 6-311++G(d,p) basis set. Wave function analysis and visualization are done using Multiwfn and VMD, respectively.

UV-visible spectra were recorded in ambient air at room temperature by a Shimadzu UV-1750 spectrophotometer, with the test film placed in a special glass sample box to avoid airborne effects. The absorption of N-DMBI and MeO-JLBI in a solution of 2×10^{-5} M in dichloromethane (DCM) was measured. The thickness of the pure and doped N2200 films used for UV-vis measurements was approximately 100 ± 5 nm, as determined by a Bruker DEKTAK-XT profilometer.

Under vacuum (4.0 × 10-8 Torr), UV photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Thermo Fisher ESCALAB 250Xi instrument with an unfiltered He I gas discharge lamp source (21.22 eV) and a monochromatic Al K α source (1486.6 eV) as excitation sources. Thin films of both polymers were spin-coated onto 1×1 cm² ITO glass substrates. The Fermi level (E_F) was determined from the equation $WF = E_{vac} - E_F$, where WF and E_{vac} denote the work function and the vacuum level, respectively. Atomic force microscopy (AFM) was performed with ScanAsyst mode on Bruker Dimension FastScan, using RTESPA-ScanAsyst-Air tips (Bruker, resonant frequency 70 kHz, spring constant 0.4 N m⁻¹, tip radius 5 nm) for the measurements. We scanned all samples at a fixed scan rate of 1 Hz and 256 samples/line at a fixed aspect ratio of 1. AFM images ($5 \times 5 \mu m$) were processed and analyzed in NanoScope Analysis 1.5 Software (Bruker, USA) to calculate roughness.

In a vacuum environment, grazing incidence wide-angle X-ray scattering (GIWAXS) measurements were conducted on pristine and doped thin films using the Xeuss 3.0 SAXS/WAXS laboratory beamline. with a Cu X-ray source (8.05 keV, wavelength 1.54 Å) and an Eiger2R 1M detector. The incident angle was 0.20° with an exposure time of 1200 seconds. The thin films for testing were spin-coated on silicon substrates under the same conditions as those on glass substrates used for electrical measurements.

3. Fabrication and Characterization of Doped Samples

3.1 Device Fabrication

Ultrasonic cleaning was firstly performed on glass substrates with deionized water, acetone, and isopropanol for 20 minutes in turn. The glass substrates were then dried with a nitrogen gun, cleaned with a UVOCS ultraviolet ozone cleaning system for 10 minutes and then transferred into a glovebox filled with N₂ (H₂O < 0.1 ppm, O₂ < 0.1 ppm). The subsequent fabrication process was all carried out in the glovebox. The N2200 solution (10 mg mL⁻¹ in *o*-dichlorobenzene) was prepared by stirring at 60°C

for 1 hour and then cooled to room temperature. The dopant solution (5 mg mL⁻¹ in *o*dichlorobenzene) was obtained by stirring at room temperature for 20 minutes. Then, the N2200:dopant blended solution with a specific dopant molar fraction was prepared by adding certain volume of dopant solution to N2200 solution. The N2200:dopant blended solution was stirred for 20 minutes at room temperature before using. Subsequently, the mixed solution was spin-coated onto glass substrates at different speeds to achieve films with varied thicknesses. The fresh-prepared films were naturally dried and activated by annealing in the glovebox.

3.2 Conductivity and Seebeck coefficient Measurement

Before electrical performance measurements, 80 nm thick parallel stripe Ag electrodes were deposited as top contacts (channel length L = 8 mm, width w = 2 mm) under a shadow mask at a pressure of 2×10^{-6} bar. In a nitrogen atmosphere, electrical conductivity (σ) was measured using the standard four-probe method on a Keithlty 2420. Conductivity was calculated as $\sigma = w / (RLd)$, where d and R represent the thickness of the annealed film and the resistance of the tested area, respectively. The conductivity of each sample was obtained from at least 4 devices.

The thicker N2200 films for Seebeck coefficient measurement were prepared by a drop-coating method due to the high resistivity of the thin film samples.³⁻⁵ The prepared N2200:dopant solution was drop-cast onto a clean glass substrate (8 mm ×18 mm) and the fresh-prepared films were placed in a uncovered petri dish for natural drying. The micrometer-thick N2200 films were obtained after annealing under optimized

conditions. The Seebeck coefficient of the doped N2200 film samples were measured simultaneously with the plane-plane four-point probe method in a helium atmosphere, employing a Cryoall CTA-3S instrument (Beijing Cryoall Science & Technology Co., Ltd., China). In Seebeck coefficient measurement, two thermocouple probes spaced approximately 6 mm apart were tightly positioned on the surface of the sample. A differential heating element generated a temperature difference (ΔT) across the sample, resulting in a thermoelectric voltage (ΔV) between the two thermocouple probes. Three different temperature differences (ΔT ranging from 2 to 4 K) were applied to generate ΔV , and the Seebeck coefficient (S = $\Delta V / \Delta T$) was extracted from the linear plot of ΔV versus ΔT .

3.3 Optimization of Doping Conditions

In Figures S15 a, b, and c, for a preset doping fraction of 20 mol%, thermal annealing was performed at 150 ± 25°C to investigate the effect of annealing time on the electrical conductivity of N2200 films doped with three different dopants (N-DMBI, JLBI, and MeO-JLBI). Specifically, the annealing conditions for N-DMBI were optimized based on reported parameters in the literature.⁶ The experimental results indicate that the conductivity of N-DMBI-doped films decreases with increasing annealing time at both 110°C and 150°C. Therefore, the same annealing conditions as previously reported in the literature were adopted to optimize the preparation of N-DMBI doped films. For JLBI and MeO-JLBI doped films, annealing at 150°C for 1 hour was chosen as the optimized condition. To mitigate the influence of varying film thickness on the

electrical properties of doped N2200 films, films ranging from 30 nm to 10 µm were prepared by adjusting spin-coating speeds and solution volumes for drop-casting. All doped films were characterized for electrical performance under optimized annealing conditions. Figure S15 d demonstrates that while there is slight fluctuation in conductivity due to different film thicknesses across the three doped films, overall conductivity changes are minimal.

3.3 Carrier Concentration and Electronics Mobility

The MIS device in this work has an architecture of indium-tin-oxide (ITO)/ion-gel insulator/fullerene derivative film/Al.⁶ We employed a mixture of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfony) imide ([EMIM][TFSI]) as the ion-gel insulator. The ion-gel solution was prepared by following the previously reported method, and then spin-coated onto a clean patterned ITO substrate with a thickness of 150-300 nm followed by annealing at 140 °C for 4 h. After spin-coating the active layer onto the insulating layer, 100 nm thick Al was deposited as the top electrode, with a testing area of 2×2 mm². The C_p -V characteristics of the MIS devices were conducted at a frequency of 10 Hz for AC bias. The carrier concentrations (n) of the semiconductor layers then can be

 $n = \frac{2}{q\varepsilon_0\varepsilon_r \left(\frac{\partial C_p^{-2}}{\partial V}\right)},$ calculated from the $C_p^{-2}-V$ characteristics by Mott-Schottky analysis: where ε_0 is the permittivity of free space, ε_r is the dielectric constant of the active layer, q is the elementary charge and C_p is the specific capacitance of the device.

4. The NMR Spectra and Mass Spectrum



Figure. S1 The ¹H NMR spectrum of 8-methoxyjulolidine-9-carboxaldehyde in CDCl₃.



Figure. S2 The ¹³C NMR spectrum of 8-methoxyjulolidine-9-carboxaldehyde in CDCl₃.



Figure. S3 The mass spectrometry of 8-methoxyjulolidine-9-carboxaldehyde.



Figure. S4 The 1H NMR spectrum of MeO-JLBI in CDCl₃.



Figure. S5 The ¹³C NMR spectrum of MeO-JLBI in CDCl₃.



Figure. S6 The mass spectrometry of MeO-JLBI.

5. Figures of the Properties and Performances



Figure. S7 The TGA cures of MeO-JLBI at a heating rate of 10 °C min⁻¹ under N_2 .



Figure. S8 The DSC curve of MeO-JLBI from 30 to 200 °C under N_2 with a heating rate of 10 °C min⁻¹.



Figure. S9 The cyclic voltammetry curve of (a) N-DMBI and (b) **MeO-JLBI** in deaerated anhydrous acetonitrile of 0.1 M Bu_4NPF_6 with a scan rate of 80 mV s⁻¹.



Figure. S10 The UV-vis spectrum of (a) N-DMBI and (b) MeO-JLBI solution in CH_2Cl_2 with the concentration of 2×10^{-5} M.



Figure. S11 The DFT Calculation energy diagram of dopants N-DMBI, JLBI, and MeO-JLBI.

Dopant	$\lambda_{onset}^{sol.}(nm)$	$E_{g}^{opt}(eV)$	HOMO ^{a)}	LUMO ^{a)}	HOMO ^{b)}	SOMO ^{b)}	LUMO ^{b)}
			^{a)} (eV)	(eV)	(eV)	(eV)	(eV)
N-DMBI	342	3.62	-4.65	-1.03	-4.61	-2.21	-0.53
JLBI	349	3.55	-4.66	-1.11	-4.58	-2.01	-0.58
MeO-	246	2 50	4.60	1.04	4 40	1.90	0.54
JLBI	340	3.38	-4.62	-1.04	-4.42	-1.89	-0.54

Table S1 Optical Properties, Electrochemical Properties, and Energy Levels of the dopants.

a) Obtained from UV-vis absorption and cyclic voltammetry; b) Calculated by the DFT



Figure. S12 Electrostatic potential (ESP) of N-DMBI, JLBI, and MeO-JLBI neutral molecule.



Figure. S13 Electrostatic potential (ESP) of polymer repeating unit anion.



Figure. S14 Surface area in each ESP range on the vdW surface of polymer anion and dopant cations. **MeO-JLBI**⁺ has a more concentrated low positive ESPs distribution and lower maximum positive ESPs compared to N-DMBI⁺ and JLBI⁺.



Figure. **S15** The (a) N-DMBI, (b) JLBI, and (c) **MeO-JLBI** doped N2200 films annealed at various temperatures and durations. (d) The average electrical conductivity of the doped N2200 films with various thickness.



Figure. S16 UV-vis absorption spectra of the annealed pristine and doped N2200 films at various doping concentrations.



Figure. S17 Mott-Schottky plots for MIS devices based on the annealed N2200 films doped with (a) N-DMBI, (b) JLBI, and (c) **MeO-JLBI** at various doping concentrations.



Figure. S18 The Arrhenius plots of temperature-dependent conductivity for the (a) N-DMBI doped, (b) JLBI doped, and (c) **MeO-JLBI** doped N2200 films at various doping concentrations.



Figure. **S19** The fits to the variable temperature conductivity data of N2200 doped with 30 mol% N-DMBI, JLBI, and **MeO-JLBI** utilized the form $\log (\alpha) = \log (\sigma^0) - (1/T)^{\alpha}$, where σ^0 represents the pre-exponential factor, and α is expressed as $(1 + d)^{-1}$. Various dimensionality exponents *d* were used: (a) *d*=0 for 0D variable range hopping, and (b) 1, (c) 2, and (d) 3 for 1D, 2D, and 3D variable range hopping, respectively.



Figure. S20 Optimized geometric configurations of charge transfer complexes.



Figure. S21 Mott-Schottky plots for the MIS devices based on the annealed (a) N-DMBI doped, (b) JLBI doped, (c) **MeO-JLBI** doped N2200 films at concentration of 30 mol% under various temperatures.



Figure. S22 GIWAXS patterns of the pristine and the N-DMBI doped N2200 films before and after annealing.



Figure. S23 GIWAXS patterns of the pristine and the JLBI doped N2200 films before and after annealing.



Figure. S24 GIWAXS patterns of the pristine and the MeO-JLBI doped N2200 films before and after annealing.

Dopant	IP			OOP						
	Face-on orientation						Edge-on orientation			
	Lamella stacking (100)			π–π stacking (010)			Lamella stacking (100)			
	FWHM (Å ⁻¹)	CCL (Å)	g	FWHM (Å ⁻¹)	CCL (Å)	g	FWH M (Å ⁻¹)	CCL (Å)	g	
Pristine	0.0612	92.33	0.197	0.400	14.14	0.199	-	-	-	
N-DMBI	0.0622	90.88	0.196	0.514	11.00	0.227	0.0601	94.09	0.190	
JLBI	0.0617	91.68	0.192	0.446	12.68	0.221	0.0620	91.16	0.190	
MeO-JLBI	0.0626	90.33	0.198	0.418	13.53	0.206	0.0595	95.07	0.189	

Table S2 The full width at half maximum (FWHM) and crystal coherence length (CCL) of N2200 films before and after doping at doping concentrations of 30 mol%.



Figure. S25 Time-dependent conductivity curves of the annealed N2200 films doped at the concentration of 30 mol% stored in N_2 -filled glove box.

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