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Photoirradiation Induced *p-n* Junction in Naphthylamine-Based Organic Photovoltaic Cells

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1. Materials and instruments

All reagents and chemicals were purchased commercially and used without further purifications unless otherwise stated. Reactions were monitored by TLC and visualized by a dual short wave/long wave UV lamp. Column flash chromatography was performed using 230-400 mesh silica gel.

1.1 NMR

NMR spectra were recorded by a Bruker BBFO-400 spectrometer with CDCl₃ as a solvent. Chemical shifts for ¹H NMR were reported as δ , parts per million, relative to the signal of CDCl₃ at 7.26 ppm. Chemical shifts for ¹³C NMR were reported as δ , parts per million, relative to the centerline signal of the CDCl₃ triplet at 77.0 ppm. Proton and carbon assignments were established using spectral data of similar compounds. The abbreviations s, br. s, d, dd, br. d, ddd, t, q, br. q, m, and br. m stand for the resonance multiplicity singlet, broad singlet, doublet, doublet of doublets, broad doublet, doublet of doublets, triplet, quartet, broad quartet, multiplet and broad multiplet, respectively.

1.2 Thermogravimetric analysis (TGA) & Fourier transform infrared (FT-IR) experiments TGA was performed on a TGA 500 thermo gravimetric analyzer by heating the samples at 20 °C min⁻¹ to 1000 °C in a nitrogen atmosphere (60 mL/min). FTIR spectra (KBr, Aldrich) were measured with a SHIMADZU IR Prestige-21 spectrometer. Samples were packed firmly to obtain transparent films.

1.3 **PXRD measurement**

PXRD studies were performed on a SHIMADZU XRD-6000 Labx diffractometer using Cu-Ka radiation at 40 kV and 300 mA with a scanning rate of 0.02° s⁻¹ (20) at room temperature.

1.4 UV absorption and fluorescence spectra

Absorption spectra were recorded on UV-3600 UV-vis-NIR spectrophotometer (Shimadzu), while emission spectra were recorded on RF-5301 PC spectrofluorophotometer (Shimadzu) with 1.0 cm path length cell.

1.5 CV measurement

Electrochemical cyclic voltammetry (CV) was performed using a Grammy electrochemical workstation in a 0.1 mol/L tetrabutylammoniumhexafluorophosphate (Bu₄NPF₆) dichloromethane (DCM) solution with a scan speed at 0.1 V/s. Pt wire and Ag/AgCl were used as the counter and reference electrodes, respectively. The concentration of DiNA and DiNAO was adjusted as 1 \times 10⁻⁴ M in chromatographic pure DCM solution for the CV measurements.

2. Experimental details

2.1 Synthesis of DiNAO

Sunlight irradiation

A 100mL conical flask equipped with a magnetic stirring bar was charged with DiNA (0.56g, 2.1mmol) and solvent (60mL). The mixture was placed under sunlight irradiation for 3-6 h. After the reaction was completed, the solvent was removed by rotary evaporation and the residue was purified by chromatography on SiO₂ (10:1, hexane/EtOAc) to provide DiNAO (476 mg, 80%) as red solid.

Visible light irradiation

A dried 25mL round bottom flask equipped with a magnetic stirring bar was charged with tris(2,2'bipyridyl)ruthenium(II) chloride hexahydrate (1.6 mg, 2.10 μ mol, 0.01 equiv), DiNA (56 mg, 0.21 mmol, 1.0 equiv), and solvent (8 mL). The mixture was placed at a distance of ~10 cm from a 15 W fluorescent lamp. After the reaction was completed as judged by TLC analysis (about 8 h), the mixture was dried over Na₂SO₄ and concentrated. The residue was purified by chromatography on SiO₂ (10:1, hexane/EtOAc) to provide DiNAO (35.7 mg, 62%) as red solid.

2.2 Sample preparation for cell devices

For solution process, the mixture of DiNA and DiNAO in o-dichlorobenzene (o-DCB, 20 mg/mL) was spin-casted onto PEDOT:PSS (poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate)) layer, where the ratio of DiNA and DiNAO depends on the conversion of the photooxidation reaction. For the thin film case, pure donor DiNA film prepared from an o-DCB solution (20 mg/mL) was spin-casted onto PEDOT:PSS layer. For separated layer method, the blended films were prepared by spin-casting the donor and acceptor in o-DCB (20 mg/mL), in which the donor and acceptor were mixed in a 1:1 weight ratio under the same conditions.

2.3 Theoretical calculations

Density functional theory calculations were performed with the Gaussian 09 program¹ using the B3LYP functional.² All-electron double- ξ valence basis sets with polarization functions 6-31G^{*} were used for all atoms.³ Geometry optimizations were performed with full relaxation of all atoms in gas phase without solvent effects.

2.4 Device fabrication

To fabricate the conventional solar cells, the ITO glass was pre-cleaned with deionized water, HPLC grade acetone and isopropanol in turn for 15 min. The organic residues were further removed by treating with UV-ozone for 1 h. Then, the ITO glass was modified by spin-coating PEDOT:PSS (30 nm) on it. After the ITO glass was dried in an oven at 150 °C for 15 min, the active layer was spin-coated on the ITO/PEDOT:PSS using a blended solution of donor (DiNA) and acceptor (DiNAO) in o-dichlorobenzene (o-DCB, 20 mg/mL), and optimized with different donor/acceptor weight ratios. Ca (20 nm) and Al (80 nm) electrodes were then thermally evaporated on the active layer under the vacuum of 1×10^{-6} Torr. The active area of the device was 0.06 cm², and the thickness of the original active films was 60±2 nm. Moreover, the thickness of active layer was remained after the following procedures. The devices were characterized in nitrogen atmosphere under the illumination of simulated AM 1.5G at 100 mW/cm² using a xenon-lamp-based solar simulator (AAA grade, XES-70S1). The current-voltage (I-V) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. The EQE measurements were performed in air using IPCE measurement system (QE-R3011, Enli Technology Co. Ltd., Taiwan) under short-circuit condition with a monochromatic light obtained from Xenon lamp, a chopper with the frequency of 133 Hz, and a lock-in amplifier.

For the thin film devices, the procedure of pre-treatment was same as described above. The only difference was in the process of spin-coating. In this case, only DiNA was spin-coated on the surface of device, and it was used for the following tests during blending. Regarding the reference experiment using a blending film with a ratio of DiNA:DiNAO = 1:1, a homogeneous

blending solution with the ratio of DiNA:DiNAO = 1:1 was prepared in advance. Then, it was directly spin-coated on the surface of device, and used for the following tests.

3. Proposed mechanism



Figure S1. Oxidation mechanism from DiNA to DiNAO under photoirradiation.

4. Optimization of reaction conditions



Figure S2. Color of the reaction solution in various solvents under different photoirradiation: (a) before sunlight irradiation, (b) after sunlight irradiation for 6h, and (c) under UV lamp.

Solvent	Irradiation	Gas	Time	Yield (%) ^[b]	
MeOH	Sunlight	Air	6h	30	
THF	Sunlight	Air	6h	11.2	
DMF	Sunlight	Air	6h	13	
MeCN	Sunlight	Air	6h	61	
CHCl3	Sunlight	Air	6h	Byproduct	
Toluene	Sunlight	Air	6h	58	
Acetone	Sunlight	Air	6h	73	
Acetone	Dark	Air	24h	Nr ^[c]	
Acetone	UV-Lamp ^[a]	Air	24h	40	
Acetone	Sunlight	O ₂	6h	80	
Acetone	Sunlight	N ₂	6h	Nr	

Table S1 The oxidation reaction under different conditions.

[a] Irradiated at 365 nm; [b] yielded by a GC vs an internal standard; [c] no reaction.

5. Structure information



Figure S3. GCMS spectra of DiNA and DiNAO to probe the oxidation reaction.



Figure S4. Comparison on ¹H NMR spectra of DiNA and DiNAO.



Figure S5. Single crystal structure and crystal packing for DiNAO. CCDC-1405312 contains the crystal data.

6. Theoretical calculation and experimental data for DiNA and

DiNAO

Table S2. Energy levels of donor (DiNA) and acceptor (DiNAO). ^{*a*}Calculations for the HOMO were based on cyclic voltammogram data using equation: $E_{HOMO} = (-4.8 + E_{ref} - E_{ox}) \text{ eV}$. ^{*b*}Values obtained from E_{HOMO} and optical bandgap, Eg = 1240 / $\lambda_{max-edge}$

	Calculation ^a		Experiment ^b	
	HOMO / eV	LUMO / eV	HOMO / eV	LUMO / eV
DiNA	-5.23	-2.31	-5.60	-2.99
DiNAO	-5.75	-3.50	-5.85	-3.78

7. Thin film device performance

Table S3. Photovoltaic characteristics of the devices based on different ratios (x) of DiNA/DiNAO under the illumination of AM $1.5G 100 \text{ mW cm}^{-2}$.

Device structure	J _{sc} [mA	V _{oc} [V]	FF%	PCE[%]
	cm-2]			
ITO/PEDOT:PSS (30 nm)/DiNA:DiNAO (x=0.06)/Ca/Al	0.86	0.49	49.58	0.21
ITO/PEDOT:PSS (30 nm)/DiNA:DiNAO (x=0.10)/Ca /Al	0.78	0.58	53.10	0.24
ITO/PEDOT:PSS (30 nm)/DiNA:DiNAO (x=0.13)/Ca/Al	1.54	0.57	48.72	0.42
ITO/PEDOT:PSS (30 nm)/DiNA:DiNAO (x=0.19)/Ca/Al	1.24	0.57	60.78	0.43
ITO/PEDOT:PSS (30 nm)/DiNA:DiNAO (x=1:1)/Ca/Al	3.50	0.63	78.42	1.73

8. Morphology study on Thin film



Figure S6. AFM images for the DiNA film (a) before photoirradiation and after photoirradiation for (b) 1h, (c) 2h, and (d) 6h.

9. Photoluminance (PL) intensity for thin film



Figure S7. PL spectra of the blend films under different time: before photoirradiation (black), and after photoirradiation for 1h (blue), 2h (pink), and 6h (red). Excitation wavelength of the films was 363 nm. Each spectrum was corrected based on the absorption of the film at the excitation wavelength.

10. Reproducibility

The reproducibility was evaluated based on the performance of all the devices. Firstly, the average value of power conversion efficiency (PCE) was calculated based on 7 devices under each condition. Then, the standard deviation of PCE was obtained to show the distribution range of PCE under each condition.



Figure S8. Statistic standard deviation of PCE for the reproducibility of solar cell devices. The plots represent the average values, and the scale bars indicate the distribution ranges of PCE.

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