Supplementary Information (SI) for New Journal of Chemistry.
This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2024

Supporting Information

Efficient Interfacial Optimization of NiO_x-based Perovskite Solar Cells Via a Butterfly-Structured Semiconductor

Zhihui Wang,[1,*] Zhe Wang,[1] Zhaolong Ma,[1] Ruifeng Chen,[1] Ting Wang,[2] Jiali Kang,[2] Guang Hu,[1,*] Xueping Zong,[2,*]

[1] *National & Local Joint Engineering Research Center for Deep Utilization Technology of Rock-salt Resource, Key Laboratory for Palygorskite Science and Applied Technology of Jiangsu Province, Huaiyin Institute of Technology, Huaian 223003, China.*

[2] *Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry and Chemical Engineering, Tianjin University of Technology, Tianjin 300384, China.*

Corresponding author:

E-mail: wangzhihui_tju@126.com

E-mail: guanghu2019@hyit.edu.cn

E-mail: xp_zong@email.tjut.edu.cn

List of Content

Number of pages: 8

Number of figures: 6

Number of tables: 4

1 Characterization.

The molecular structure was characterized utilizing a Bruker AV400 Spectrometer operating at 400 MHz and 100 MHz for ^{1}H NMR and ^{13}C NMR, respectively. UV-vis absorption spectra were recorded with a Shimadzu UV-2600 absorption spectrophotometer. Fluorescence emission spectra were recorded with a Hitachi F-4500 FL Spectrophotometer. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 F3 differential scanning calorimeter with a scanning from -40 °C to 300 °C at a rate of 10 °C min^{-1} under a nitrogen atmosphere. Ultraviolet photoelectron spectroscopy (UPS) was carried out using a Thermo ESCALAB XI+ analysis system.

Hole mobility was evaluated using the space-charge-limited current (SCLC) method with a device configuration of ITO/PEDOT:PSS/HTMs/Ag.[1, 2] The hole mobility was calculated according to the formula below:

$$J = 9\mu\varepsilon_0\varepsilon_r V^2/(8d^3)$$

Here, $\varepsilon_r \approx 3$ represents the average dielectric constant of the film, ε_0 is the vacuum permittivity of the free space ($8.85*10^{-12}$ F/m), μ is the carrier mobility, d signifies the thickness of HTM film, and V stands for the applied voltage.

The SEM images were obtained by a JEOL JSM-7800 scanning electron microscope. The XPS spectra were acquired with a Kratos X-ray photoelectron spectrometer (AXIS Ultran HAS), which is equipped with monochromatic Al Kα (1,486.6 eV) and non-monochromatic HeI (21.22 eV) sources. X-ray diffraction (XRD) characterization was performed using a Bruker D8 X-ray diffractometer

(Bruker D8 Advance diffractometer, Germany). Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) were measured through Spectrofluorometer FS5 with excitation at 500 nm.

The trap-state density (N_t) was obtained using a SCLC method by collecting the *I-V* characteristics of devices under dark conditions.[3] The N_t was calculated using the formula below:

$$N_t = 2\varepsilon_0\varepsilon_r V_{TFL} / qL^2$$

in which V_{TFL} stands for the trap filling limit voltage, ε_0 represents the vacuum permittivity of the free space that is generally specified as 8.85×10^{-12} F m^{-1}; ε_r signifies the material dielectric constant (~32). L is the thickness of perovskite films, and q is 1.6×10^{-19} C.

J-V curves were recorded by a Keithley 2400 source/meter under AM 1.5 illustration (100 mW cm^{-2}), calibrated with a standard Si photodiode detector.

2 Device Fabrication

A structure of ITO/NiO_x/Y34/$MAPbI_3$/$PC_{60}BM$/Bathocuproine (BCP)/Ag was utilized for the fabrication of perovskite solar cells (PSCs). The cleaned ITO glass substrates were processed in an ultraviolet Ozone cleaner for 30 min. NiO_x nanoparticles were dispersed in deionized water at a concentration of 20 mg/mL. The freshly prepared NiO_x ink was spin-coated onto the ITO substrate at 2000 rpm for 30 s, and then annealed at 120 °C for 15 min in ambient air. Subsequently, Y34 in CB with a concentration of 5 mg mL^{-1} was spin-coated onto the substrate at 3000 rpm for 30 s and annealed at 100 °C for 10 min.

The perovskite layers were fabricated through a one-step spin-coating procedure. PbI_2 (466 mg) and MAI (159 mg) were added into 1 mL mixed solution of DMSO (71 uL) and DMF (639 uL), and further stirred for 30 min at 60 °C. Afterwards, the filtered precursor solution was spin-coated on the NiO_x layer at 4000 rpm for 25 s. 110 uL of CB was poured on the spinning substrate. The substrates were heated at 100 °C for 10 min, followed by spin-coating a solution of $PC_{61}BM$ (20 mg/mL in CB) at 3000 rpm for 30 s. Subsequently, a BCP solution (0.5 mg/mL in IPA) was deposited at 4000 rpm for 40 s as a buffer layer. Finally, the electrode Ag with a thickness of 100 nm was coated on the top of BCP film using thermal evaporation.

3 Figures.

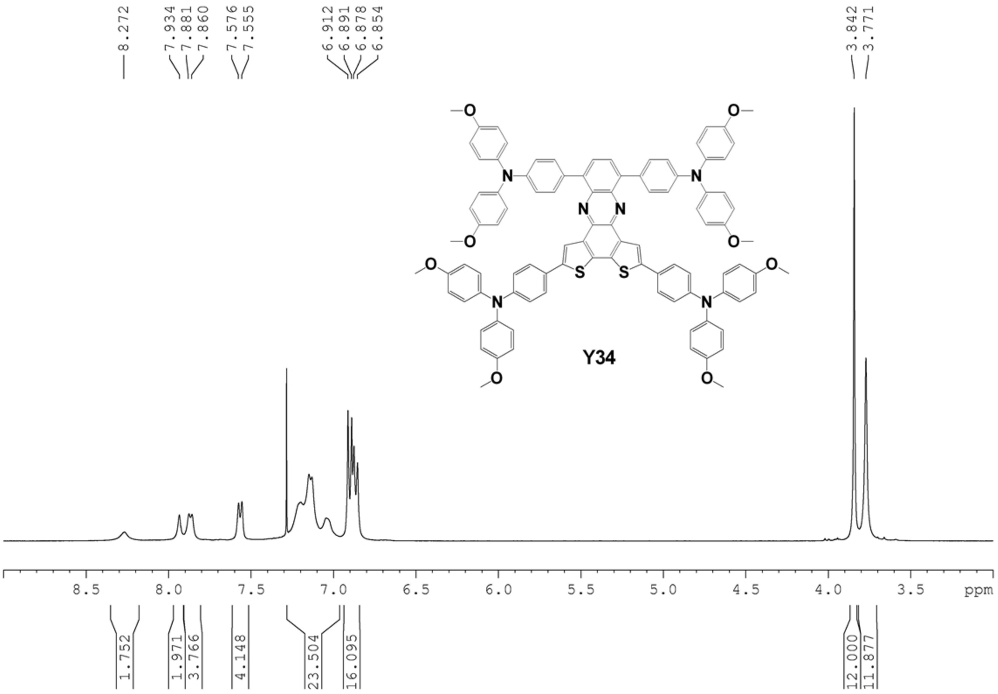

Figure S1. ^{1}H NMR spectra of Y34 ($CDCl_3$).

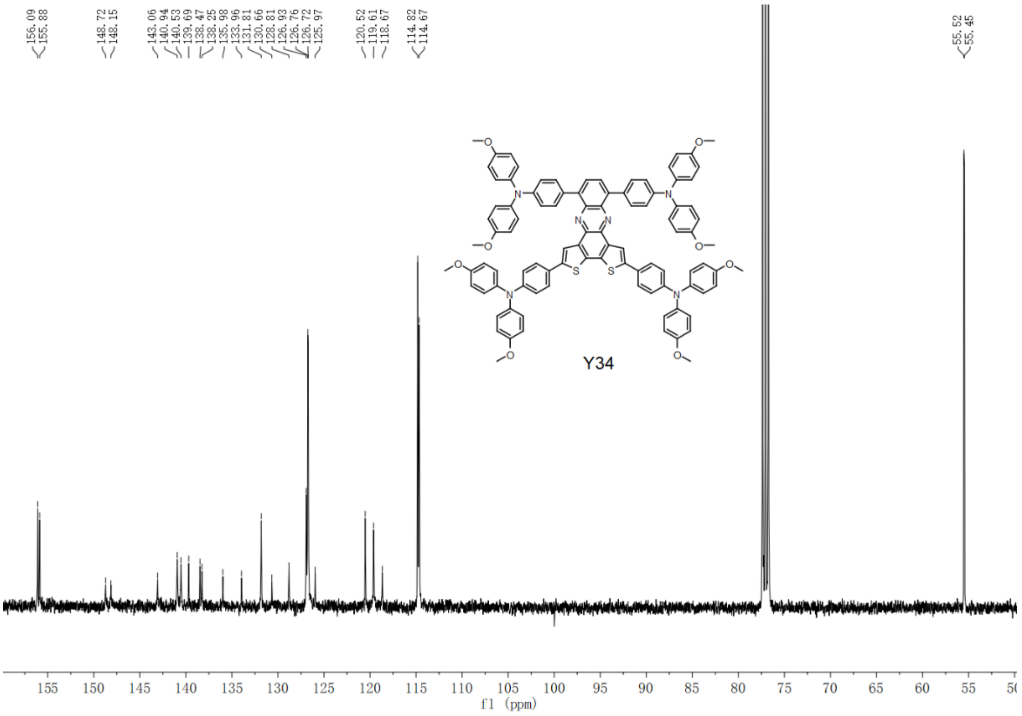

Figure S2. ^{13}C NMR spectra of Y34 ($CDCl_3$).

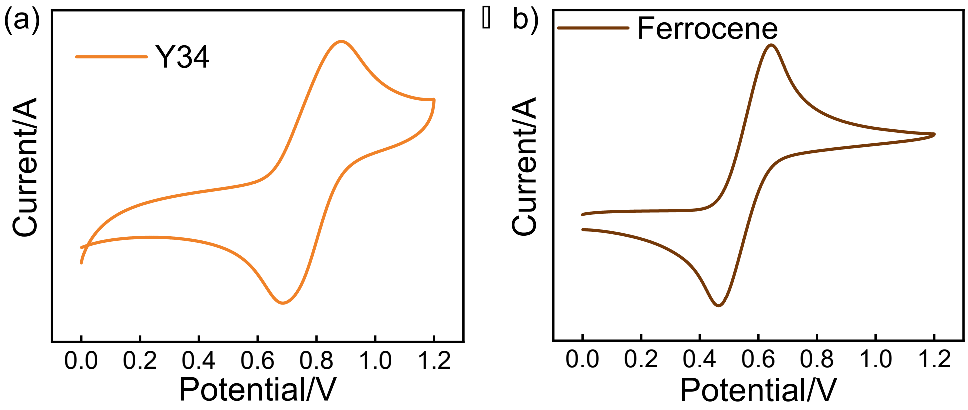

Figure S3. Cyclic voltammetry curves of (a) Y34 and (b) ferrocene in CH_2Cl_2 solution.

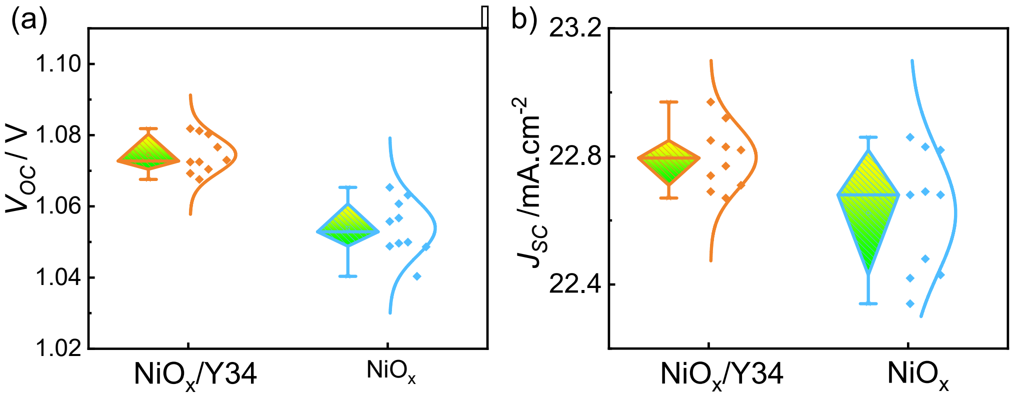

Figure S4. The statistics of PSCs based on NiO$_x$ and NiO$_x$/Y34. (a) V_{OC} and (b) J_{sc}.

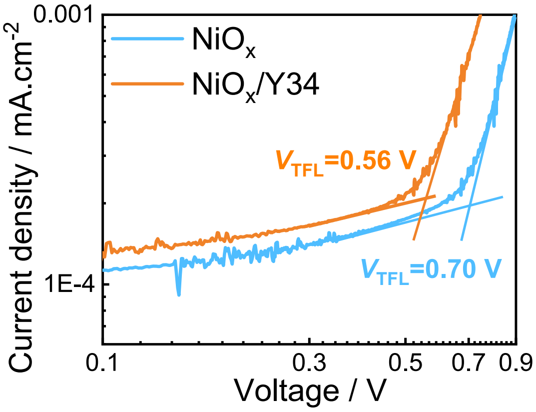

Figure S5. Trap density measured utilizing the SCLC method.

4 Tables.

Table S1. Electrochemical and optical data of Y34.

HTM	λ_{int} /nm	E_g /eV$^{(a)}$	E_{HOMO} /V$^{(b)}$	E_{HOMO} /eV$^{(c)}$	E_{LUMO} /eV$^{(d)}$
Y34	441	2.81	0.76	-5.26	-2.45

$^{(a)}$ $E_g = 1240/\lambda_{\mathrm{int}}$. λ_{int} is the intersection point of normalized UV-visible absorption curve and the fluorescence emission curve.

$^{(b)}$ The redox potential obtained from the CV plots and it was standardized with ferrocene.

$^{(c)}$ E_{HOMO} *vs* (Ag/AgCl) (eV) = -($E_{\mathrm{HOMO}}{}^{(b)}$ + 4.5].

$^{(d)}$ E_{LUMO} (eV) = $E_{\mathrm{HOMO}}{}^{(c)}$ + E_g (eV).

Table S2. Calculated result of repeatability test.

HTMs	V_{oc} ^{a}/V	J_{sc} ^{a}/mA cm^{-2}	FF ^{a}/%	PCE ^{a}/%
NiO_x	1.054±0.007	22.66±0.197	72.75±1.673	17.37±0.488
NiO_x/Y34	1.075±0.005	22.78±0.079	75.03±0.591	18.36±0.174

Table S3. Fitted carrier lifetime of perovskite films measured by TRPL measurements.

Sample	τ_1 / ns	A_1 /%	τ_2 / ns	A_2/%	τ_{avg} /ns
$MAPbI_3$	28.98	91.61	321.65	4.39	176.53
NiO_x	21.11	90.69	207.25	9.31	114.55
NiO_x/Y34	12.92	90.24	143.21	9.75	83.94

Note: The average lifetime can be calculated with the equation of: $\tau_{avg} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$, where parameters A_1 and A_2 are the amplitude fraction foreach decay component, and τ_1 and τ_2 represent the time constant of the two types of decay.

Table S4. Fitted XRD ratio of perovskite films deposited on different substrates.

Sample	ITO/NiO_x/Perovskite	NiO_x/Perovskite/Y34	ITO/Perovskite
FWHM	0.29826	0.26693	0.34139

4 References.

1. Choi, H.; Lee, J.; Kim, H.; Kim, J.; Park, T.; Song, S., Water-Repelling Dopant-Free Hole-Transporting Materials for Stable and Efficient Planar Perovskite Solar Cells. *ACS Sustainable Chemistry & Engineering* **2022,** *10* (45), 14948-14954.

2. Cheng, Y.; Fu, Q.; Zong, X.; Dong, Y.; Zhang, W.; Wu, Q.; Liang, M.; Sun, Z.; Liu, Y.; Xue, S., Coplanar Phenanthro[9,10-d]Imidazole Based Hole-transporting Material Enabling over 19%/21% Efficiency in Inverted/Regular Perovskite Solar Cells. *Chemical Engineering Journal* **2021,** *421*, 129823.

3. Sun, X.; Zhang, C.; Gao, D.; Zhang, S.; Li, B.; Gong, J.; Li, S.; Xiao, S.; Zhu, Z.; Li, Z. a., Boosting Efficiency and Stability of NiO_x-Based Inverted Perovskite Solar Cells Through D-A Type Semiconductor Interface Modulation. *Adv. Funct. Mater.* **2024,** *34* (25), 2315157.