Supporting Information for:

Diketopyrrolopyrrole derivatives for efficient NiO-based dyesensitized solar cells :

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1. Experimental Section

¹H and ¹³C NMR spectra were recorded on a *Bruker ARX 300 MHz*, AVANCE 400 BRUKER or AVANCE III 500 BRUKER. Chemical shifts for ¹H NMR spectra are referenced relative to residual protium in the deuterated solvent (CDCl₃ δ = 7.26 ppm for ¹H and δ = 77.16 ppm for ¹³C; THF-d8 δ = 3.57, 1.72 ppm for ¹H and δ = 67.21, 25.31 ppm for ¹³C; CD₃OD δ = 3.31 ppm for ¹H and $\delta = 49.00$ ppm for ¹³C). Spectra were recorded at room temperature, chemical shifts are written in ppm and coupling constants in Hz. High-resolution mass (HR-MS) spectra were obtained either by electrospray ionization coupled with high resolution ion trap orbitrap (LTQ-Orbitrap, ThermoFisher Scientific,) or by MALDI-TOF-TOF (Autoflex III de Bruker), both working in ion-positive mode. Electrochemical measurements were performed with a potentiostat-galvanostat AutoLab PGSTAT 302N controlled by resident GPES software (General Purpose Electrochemical System 4.9) using a conventional single-compartment three-electrode cell. The working electrode was a glassy carbon or a platinum electrode. The auxiliary was a Pt plate of 1 cm² and the reference electrode was the saturated potassium chloride calomel electrode (SCE). The supporting electrolyte was 0.1 N Bu₄NPF₆ in CH₂Cl₂ and solutions were purged with argon before the measurements. All potentials are quoted relative to SCE. In all the experiments the scan rate was 100 mV/s. UV-Visible absorption spectra were recorded on a UV-2401PC Shimadzu spectrophotometer. Fluorescence spectra were recorded on a SPEX Fluoromax fluorimeter. Infrared spectra (IR) were recorded on a BRUKER Vector 22 spectrometer; frequencies are reported in cm⁻¹. Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735 Kieselgel 60F₂₅₄. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh). Chemicals were purchased from Sigma-Aldrich or Alfa Aesar and used as received.

1.a. Theoretical Calculations

All simulations have been achieved with the Gaussian09 program, using Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT), for the ground and excited state properties, respectively. The computational protocol proceeds through a four step strategy that is efficient to determine the charge transfer features of rod-like organic dyes: 1) the ground-state geometrical parameters have been determined at the PBE0/6-311G(d,p) [1], via a force-minimization process using a SCF convergence threshold of 10^{-10} a.u.; 2) the vibrational

spectrum of each derivative has been determined analytically at the same level of theory, that is PBE0/6-311G(d,p), and it has been checked that all structures correspond to true minima of the potential energy surface; 3) the first fifteen low-lying excited-states have been determined within the vertical TD-DFT approximation using the CAM- B3LYP/6-311++G(d,p) [2] level of approximation with a tight SCF convergence threshold (at least 10^{-7} a.u.); 4) the charge-transfer parameters have been estimated with the procedure defined by Ciofini, Le Bahers and coworkers [3] using the CAM-B3LYP electronic densities. It proposes to evaluate the distance separating the barycenters of the electron density gain/depletion upon electron transition. All calculations systematically include a modelling of bulk solvent effects (here CH₂Cl₂) through the Polarizable Continuum Model (PCM) [4]. During the simulations, the long alkyl chains such as alkyl moiety have been replaced by methyl groups in order to lighten the computational burden.

1.b. Fabrication of the dye-sensitized solar cells

Conductive glass substrates (F-doped SnO₂) were purchased from Pilkington (TEC8, sheet resistance 8 Ω /square). Conductive glass substrates were successively cleaned by sonication in soapy water, then ethanol for 10 min before being fired at 450 °C for 30 min. Once cooled down to room temperature, FTO plates were rinsed with ethanol and dried in ambient air. NiO electrodes were prepared by screen-printing of a NiO paste on clean FTO substrates, using a commercial semiautomatic screen printer. The NiO screen-printing paste was produced by preparing a slurry of 3 g of NiO nanopowder (Inframat) suspended in 10 mL of distilled ethanol and ball-milled (500 rpm) for 24 h. The resulting slurry was mixed in a round-bottom flask with 10 ml of 10 wt% ethanolic ethyl cellulose (Sigma Aldrich) solution and 20 ml terpineol, followed by slow ethanol removal by rotary evaporation. The dried film was first calcined in air at 400 °C for 0.5 h followed by sintering at 550 °C for 10 min. The prepared NiO electrodes were soaked while still hot (80 °C) in a 0.16 mM solution of each dye during 16 h. A mixture of distilled dichloromethane and tetrahydrofuran was used (2/1, v/v) for new dyes bath preparation. In case of co-adsorption, required quantity of chenodeoxycholic acid (0.8 mM) was added to the bath before soaking. For PMI-NDI bath, distilled acetone was used (0.25 mM).

Electrolyte used are composed of: 0.5 M 1,2-dimethyl-3-butylimidazolium iodide, 0.5 M LiI, 0.1 M I₂, 0.5 M 4-*tert*-butylpyridine and 0.1 M guanidinium thiocyanate in acetonitrile for I₃⁻/ Γ electrolyte and 0.1 M Co^{II}(dtb-bpy)₃, 0.1 M Co^{III}(dtb-bpy)₃ and 0.1M LiClO₄ in propylene carbonate for cobalt complex as redox shuttle. Counter electrode were prepared by chemical deposition of platinum from hexachloroplatinic acid in distilled isopropanol (2 mg per mL). The two electrodes were placed on top of each other using a thin transparent film of Surlyn polymer (DuPont, 25 µm) as a spacer to form the electrolyte space. The empty cell was tightly held, and the edges were heated to 110 °C to seal the two electrodes together. A drop of electrolyte was introduced through a predrilled hole in the counter electrode by vacuum backfilling, and was sealed afterward. The cell had an active area of *ca*. 0.25 cm².

The current-voltage characteristics were determined by applying an external potential bias to the cell and measuring the photocurrent using a Keithley model 2400 digital source meter. The solar simulator is an Oriel Lamp calibrated to 100 mW/cm². The overall conversion efficiency (η) of the photovoltaic cell is calculated from the integral photocurrent density (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor of the cell (FF), and the intensity of the incident light (I_{Ph}).

2. Additional theoretical results

	$\lambda_{max}(f)$	H (eV)	L (eV)	$\mu_0(D)$	$d_{CT}(Å)$	$q_{CT}(e)$	$\mu_{CT}(D)$
DPP-Br	472 (0.86): H->L	-6.86	-2.07	3.45	0.59	0.38	1.09
DPPCN ₂	503 (1.48): H->L; H->L+1	-6.83	-2.43	9.69	1.99	0.43	4.13
	392 (0.54): H-1->L; H->L+1				2.90	0.46	6.44
DPP-NDI	490 (1.24): H->L+1	-6.78	-2.64	3.60	0.27	0.39	0.50

Table S1: Computed transition wavelengths and oscillator strength, OM blend for each transition, HOMO and LUMO energies, ground-state dipole moment, CT distance, charge and dipole moments computed with TD-DFT.

For all molecules, we show below the structure, the density difference plots (red regions: gain of density, blue regions: loss of density) and the frontier orbitals.

2.a. Molecule DPP-Br

Structure

Δρ 490 nm transition

L

H



2.b. Molecule DPPCN₂



2.c. Molecule DPP-NDI



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3. Synthesis of the sensitizers



Scheme 1. Synthesis of **DPP-Br**, **DPPCN**₂ and **DPP-NDI**. Reagents and conditions : i) 5-carboxythiophene-2boronic acid pinacol ester, Pd(PPh₃)₄, Na₂CO₃, THF/H₂O (2/1), 22%; ii) 5-formyl-2-thienylboronic acid, Pd(PPh₃)₄, Na₂CO₃, THF:H₂O, 34%; iii) NDI-ethynyl, Pd(PPh₃)₄, CuI, Et₃N, THF, 48%; iv) 5-carboxy thiophene-2-boronic acid pinacol ester, Pd(PPh₃)₄, Na₂CO₃, THF/H₂O (2/1), 31%; v) malononitrile, Et₃N, CH₃CN, reflux, 61%.

Compounds $1^{5,6}$ and **NDI-Ethynyl**⁷ were prepared according to literature methods.

5-(4-(3-(4-bromophenyl)-2,5-di(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4-dione)phenyl) thiophene-2-carboxaldehyde (2)⁸

Compound **1** (199 mg, 0.30 mmol), Pd(PPh₃)₄ (24 mg, 0.02 mmol), and sodium carbonate (1.02 g, 5.3 mmol) were solubilised in 4 mL of THF and 2 mL of H₂O, under argon atmosphere. The blend was heated at 45 °C for 0.5 h and then a solution of 5-formyl-2-thienylboronic acid (53 mg, 0.34 mmol) in 4 mL of THF was added. The temperature was increased to 80 °C and maintained for 16 h. Once back to room temperature, water was poured and the crude extracted with dichloromethane. After two aqueous washings, the organic phase was dried on MgSO4, filtered and concentrated to give a red solid. The product was then purified on column chromatography (silica gel, dichloromethane). A yellow ring corresponding to the starting material was collected first, followed by an orange fraction corresponding to pure compound **2** (71 mg, 34%).

¹**H** NMR (300 MHz, CDCl₃): $\delta_{\rm H} = 9.91$ (1H, s), 7.84 (2H, d, J = 8.6 Hz), 7.76 (3H, m), 7.76 (2H, d, J = 8.5 Hz), 7.62 (4H, bs), 7.48 (1H, d, J = 4.0 Hz), 3.75 (2H, d, J = 7.8 Hz), 3.71 (2H, d, J = 7.6 Hz), 1.45 (2H, m), 1.08 (16H, m), 0.74 (12H, m).

¹³**C** NMR (75 MHz, CDCl₃): $δ_c = 182.9$, 162.6, 152.7, 147.9, 143.4, 137.4, 135.4, 132.2, 130.2, 129.6, 129.2, 127.3, 126.7, 125.7, 125.2, 110.3, 110.2, 45.2, 45.1, 38.7, 30.4, 28.4, 23.9, 23.0, 14.1, 10.6.

MALDI-TOF: m/z: Calculated for: 701.2407 [MH]⁺, Found: 701.2419 [MH]⁺, $\Delta = 1.7$ ppm.

Compound 2 (70.0 mg, 0.100 mmol), Pd(PPh₃)₄ (8.0 mg, 0.007 mmol), and sodium carbonate (166 mg, 1.50 mmol) were solubilised in 3.0 mL of THF and 1.3 mL of H₂O, under argon atmosphere. The blend was heated at 45 °C for 0.5 h and then a solution of 5-carboxythiophene-2-boronic acid pinacol ester (50.7 mg, 0.200 mmol) in 2.0 mL of THF was added. The temperature was increased to 80 °C and maintained for 16 h. Once back to room temperature, water was poured and the crude extracted with dichloromethane. After two aqueous washings, the organic phase was dried on MgSO4, filtered and concentrated to give a red solid. The product was then purified on column chromatography (silica gel, dichloromethane/methanol, 9/1) to afford the title compound as a red solid (23 mg, 31%).

¹**H** NMR (400 MHz, CDCl₃): $\delta_{\rm H} = 9.87$ (1H, s), 7.93 (4H, m), 7.80 (5H, m), 7.67 (1H, bs), 7.62 (1H, d, J = 3.8 Hz), 3.83 (4H, bd, J = 9.91 Hz), 1.45 (2H, m), 1.12 (16H, m), 0.76 (12H, m).

¹³C NMR (100 MHz, CDCl₃): $\delta_c = 182.8$, 162.6, 152.3, 148.2, 147.7, 144.5, 137.9, 136.4, 135.8, 134.6, 130.4, 129.9, 129.2, 126.7, 126.3, 126.0, 125.4, 110.7, 45.0, 39.3, 30.1, 28.9, 23.5, 14.1, 10.6.

MALDI-TOF: m/z: Calculated for: 749.3077 [MH]⁺, Found: 749.3067 [MH]⁺, $\Delta = 1.3$ ppm.

5-(4-(4-(4-(5-(2,2-dicyanovinyl)thiophen-2-yl)phenyl)-2,5-bis(2-ethylhexyl)-3,6-dioxo-2, 3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)phenyl)thiophene-2-carboxylic acid(DPPCN₂) DPP-CN₂ intermediate (23 mg, 0.031 mmol) and malononitrile (6.0 mg, 0.092 mmol) were placed in dry acetonitrile (4 mL) before distilled triethylamine (few drops) was added. The solution was refluxed for 1 h. The solution's colour turned to deep red and the degree of advancement was followed by TLC. After concentration, the crude was purified by flash column chromatography (silica gel, dichloromethane/methanol, 9/1) to furnish a red solid (15 mg, 61%).

¹**H NMR** (400 MHz, THF-d8): $\delta_{\rm H} = 8.26$ (1H, s), 7.98 (2H, d, J = 8.44 Hz), 7.94 (2H, d, J = 8.40 Hz), 7.89 (2H, d, J = 8.40 Hz), 7.84 (1H, d, J = 4.16 Hz), 7.80 (2H, d, J = 8.28 Hz), 7.71 (1H, d, J = 3.88 Hz), 7.68 (1H, d, J = 3.88 Hz), 7.50 (1H, d, J = 3.88 Hz), 3.84 (4H, dd, J = 6.95 Hz and J = 2.49 Hz), 1.48 (2H, m), 1.13 (16H, m), 0.79 (6H, t, J = 6.30 Hz), 0.74 (6H, t, J = 7.34 Hz).

¹³**C NMR** (100 MHz, CDCl₃): $\delta_c = 162.7$, 162.6, 154.6, 151.7, 149.8, 148.4, 147.4, 140.7, 136.5, 136.3, 135.0, 134.7, 130.6, 130.4, 129.3, 127.0, 126.4, 125.4, 114.7, 114.1, 111.1, 110.7, 78.0, 45.1, 39.4, 31.1, 30.4, 29.0, 24.5, 23.5, 14.1, 10.5.

FT-IR (KBr, cm⁻¹): 2223.6 (CN).

MALDI-TOF: m/z: Calculated for: 797.3190 [MH]⁺, Found: 797.3159 [MH]⁺, Δ = 3.9 ppm.

5-(4-(4-(4-bromophenyl)-2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)phenyl)thiophene-2-carboxylic acid (DPP-Br)

Compound **1** (392 mg, 0.587 mmol), Pd(PPh₃)₄ (47.3 mg, 0.041 mmol), and sodium carbonate (111 mg, 1.05 mmol) were solubilised in 7.8 mL of THF and 3.9 mL of H₂O, under argon atmosphere. The blend was heated at 45 °C for 0.5 h and then a solution of 5-carboxythiophene-2-boronic acid pinacol ester (114 mg, 0.663 mmol) in 7.8 mL of THF was added. The temperature was increased to 80 °C and maintained for 16 h. Once back to room temperature, water was poured and the crude extracted with dichloromethane. After two aqueous washings, the organic phase was dried on MgSO4, filtered and concentrated to give a red solid. The product was then purified on column chromatography (silica gel, dichloromethane/methanol, 9/1) to afford the title compound as a red solid (90 mg, 22%).

¹**H** NMR (400 MHz, MeOD-CDCl₃ (1/1, v/v)): $\delta_{\rm H}$ = 7.68 (2H, d, J = 8.2 Hz), 7.66 (1H, bs), 7.60 (2H, d, J = 8.2 Hz), 7.50 (4H, bs), 7.25 (1H, bs), 3.67 (4H, dd, J = 16.00 Hz and J = 6.90 Hz), 1.32 (2H, m), 1.04 (16H, m), 0.71 (12H, m).

¹³C NMR (100 MHz, MeOD-CDCl₃(1/1, v/v)): $\delta_c = 163.2$, 163.0, 149.3, 148.7, 148.4, 136.8, 134.2, 132.4, 130.7, 130.0, 128.2, 127.6, 126.2, 126.1, 125.2, 110.1, 109.9, 45.3, 45.1, 38.9, 38.8, 30.8, 28.7, 24.3, 23.2, 14.1, 10.7.

MS-ESI(+): m/z: Calculated for: 717.2356 $[MH]^+$, Found: 717.2348 $[MH]^+$, $\Delta = 1.1$ ppm.

DPP-NDI

Under an argon atmosphere **DPP-Br** (40 mg, 0.056 mmol), copper iodide (1 mg, 0.003 mmol) and **NDI-ethynyl** (45 mg, 0.095 mmol) were mixed in anhydrous tetrahydrofuran (6 mL) with triethylamine (3 mL). The resulting solution was freed from O_2 by three freeze-pump-thraw cycles and Pd(PPh₃)₄ (6.4 mg, 0.006 mmol) was added. Then the solution was heated to reflux for 16 h. Solvent was removed under vacuum and the crude was purified by flash column chromatography (silica gel, dichloromethane/methanol, 97/3) to afford a red solid (39.2 mg, 63%).

¹**H** NMR (500 MHz, CDCl₃): $\delta_{\rm H} = 8.40$ (4H, m), 7.67 (3H, bd, J = 6.58 Hz), 7.62 (4H, d, J = 7.46 Hz), 7.48 (2H, d, J = 6.58 Hz), 7.39 (2H, d, J = 7.24 Hz), 7.21 (3H, bd, J = 7.68 Hz), 4.21 (2H, bt, J = 7.13 Hz), 3.72 (4H, m), 1.79 (2H, m), 1.25-1.49 (16H, m), 1.04-1.19 (14H, m), 0.90 (3H, t, J = 7.12 Hz), 0.66-0.83 (12H, m).

¹³C NMR (125 MHz, CDCl₃): $δ_c = 162.8$, 162.5, 148.4 135.4, 134.3, 132.9, 131.6, 130.9, 130.6, 129.8, 129.0, 128.9, 128.2, 128.1, 127.0, 126.9, 126.7, 126.5, 125.5, 125.4, 124.2, 109.4, 91.0, 90.5, 44.7, 41.3, 38.3, 32.1, 32.0, 31.9, 30.6, 29.8, 29.7, 29.5, 29.4, 29.3, 28.4, 28.2, 27.3, 24.0, 23.1, 23.0, 22.8, 14.2, 14.1, 10.6.

MS-ESI(+): m/z: Calculated for: 1115.4981 [MH]⁺, Found: 1115.4987 [MH]⁺, $\Delta = 0.6$ ppm.



Figure S1. Fluorescence spectra of DPP-Br and DPP-NDI in dichloromethane at 298K.

3. Electrochemical Impedance Spectroscopy experiments

Electrochemical impedance spectroscopy (EIS) experiments were carried out on the DSSC prepared with **DPP-NDI** to access the charge transfer of the recombination process with a Potentiostat model VSP from Bio-Logic Science Instruments. The DSSC was examined in the dark and under 1 sun illumination at V_{oc} in the frequency range of 10 MHz to 50 mHz. The photocathode was connected to the working electrode and the anode to the counter and reference electrodes. As shown in Figure S2, two semicircles were observed: a smaller first circle observed at the region of high frequencies assigned to the charge transfer process at the interface counter-electrode/electrolyte. A second larger semicircle observed in the middle frequency region was attributed to the charge transfer of the recombination process at the interface NiO-DPP-NDI/electrolyte.



Figure S2: EIS Nyquist plots of DSSC recorded at open circuit under 1 sun (*) and in the dark (o).

The hole lifetime τ_n in NiO layer was obtained from the relation $\tau_n = R_{CT} C_{\mu}$ where R_{CT} and C_{μ} are respectively the electron transfer resistance and the chemical capacitance at NiO/dye/electrolyte interface. All values of bias voltage were corrected by subtracting IR ohmic drop. Using the transmission line model, the trend of the hole lifetime vs the applied bais potential was then obtained from the fitting EIS results. The EIS data was fitted using Zim-Fit (Bio-Logic Science Instrument France) analysis software.





Figure S3. Structures and names of some compounds mentioned in the study.

4. References

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