

Supporting information materials for
Improved efficiency of PbS quantum dot sensitized NiO
photocathodes with naphthalene diimide electron acceptor bound to
the surface of the nanocrystals

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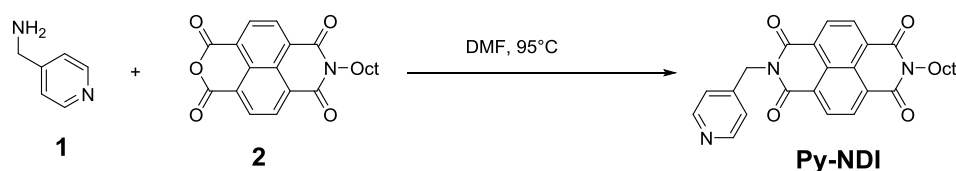
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Synthesis of the ligand py-NDI

Generalities

¹H, ¹³C and ³¹P NMR spectra were recorded on an *AVANCE 300 UltraShield BRUKER* and *AVANCE 400 BRUKER*. Chemical shifts for ¹H and ¹³C 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) or to an internal reference (TMS, δ = 0 ppm for both ¹H and ¹³C). NMR 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, Bruker), working in ion-positive or ion-negative mode. Electrochemical measurements were made under an argon atmosphere in the mixture CH₂Cl₂/DMF: 95/5 with 0.1 M Bu₄NPF₆. Cyclic voltammetry experiments were performed by using a SP300 Bio-Logic potentiostat/galvanostat. A standard three-electrode electrochemical cell was used. Potentials were referred to a saturated calomel electrode as internal reference. All potentials are quoted relative to SCE. The working electrode was a glassy carbon disk and the auxiliary electrode was a Pt wire. In all the experiments the scan rate was 100 mV·s⁻¹.

Chemicals were purchased from Sigma-Aldrich or Alfa Aesar and used as received. 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). NDI derivative **2** as prepared according to literature.[1]



Compound **2** (582 mg, 1.53 mmol, 1.0 eq) was dissolved in 25 mL of dry DMF under argon. The solution was heated at 120°C during 15min. (4-aminomethyl)-pyridine **1** (332 mg, 3.07 mmol, 2.0 eq) in dry DMF (5 mL) was added dropwise in the reaction mixture (over 10 min). The solution was stirred at 95°C overnight. The solvent was removed by evaporation and the residue taken up in dichloromethane. The organic layer was washed with distilled water (5x), dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The resulting product was purified by column chromatography (eluent: dichloromethane/methanol, 99/1, v/v). The desired product **Py-NDI** was obtained in 46% yield (330 mg). ¹H NMR (300 MHz, CDCl₃, 25°C), δ (ppm): 8.77 (s, 4H), 8.55 (br d, J=4.8 Hz, 2H), 7.38 (d, J=5.7 Hz, 2H), 5.38 (s, 2H), 4.18 (m, 4H), 3.91 (t, J=6.3 Hz, 4H), 1.73 (m, 2H), 1.26-1.41 (m, 10H), 0.86 (t, J= 6.6 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃, 25°C), δ (ppm): 162.8, 162.7, 150.2, 145.1, 131.4, 131.0, 127.1, 128.8, 126.1, 123.4, 43.0, 41.1, 31.8, 29.3, 29.2, 28.1, 27.1, 22.6, 14.1. HRMS (MALDI, Dithranol/CH₃CN) m/z: [M+H]⁺ calculated for C₂₈H₂₈N₃O₄, 470.2074; found, 470.2083. Δ= 1.9 ppm.

Fabrication of solar cell

Conductive glass substrates (F-doped SnO₂, purchased from Pilkington (TEC15, sheet resistance 15 Ω/square) 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. The PbS quantum dots were prepared according to the procedure previously reported.[2, 3]

NiO dense layer were prepared by spin-coating a nickel acetate (0.5M) with (0.5M) ethanolamine in methoxyethanol solution at 2000 rpm, 30s followed by thermal treatment at 500°C, 0.5h. Thickness of NiO dense layer (30±5nm). Then, NiO mesoporous layer deposited on this layer by screen-printing by using a commercial semiautomatic screen printer. The NiO screen-printing paste was produced by preparing a slurry of 3 g of NiO nanopowder (Inframmat) 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 calcined in air at 400 °C for 0.5 h. The prepared NiO electrodes were soaked in 20 mM Ni(CH₃COOH)₂ with 1% tetraethanolamine in ethanol solution for 30 min at 60°C followed by ethanol rinsing at 60°C during 30 min and drying at 120°C, 2h. The thickness of NiO films (~3.5 μm).

NiO electrodes were treated with 35% MPA in acetonitrile for 3min and dried in air. The film was immersed in PbS CQDs solution (50mg/ml) for overnight. The NiO-PbS films were passivated with CTAB (cetyltrimethylammonium bormide) in methanol (10mg/ml) for 5 min and rinsed with methanol to remove CTAB excess. This process was repeated three time to increase the QDs loading and remove more the isolate ligands of oleic acid. Then, the PbS-TBAI/NiO sample was socked with Py-NDI solution (1mg/ml in toluene) during 2h and rinsing with toluene.

Electrolyte used are composed of 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 (10 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}).

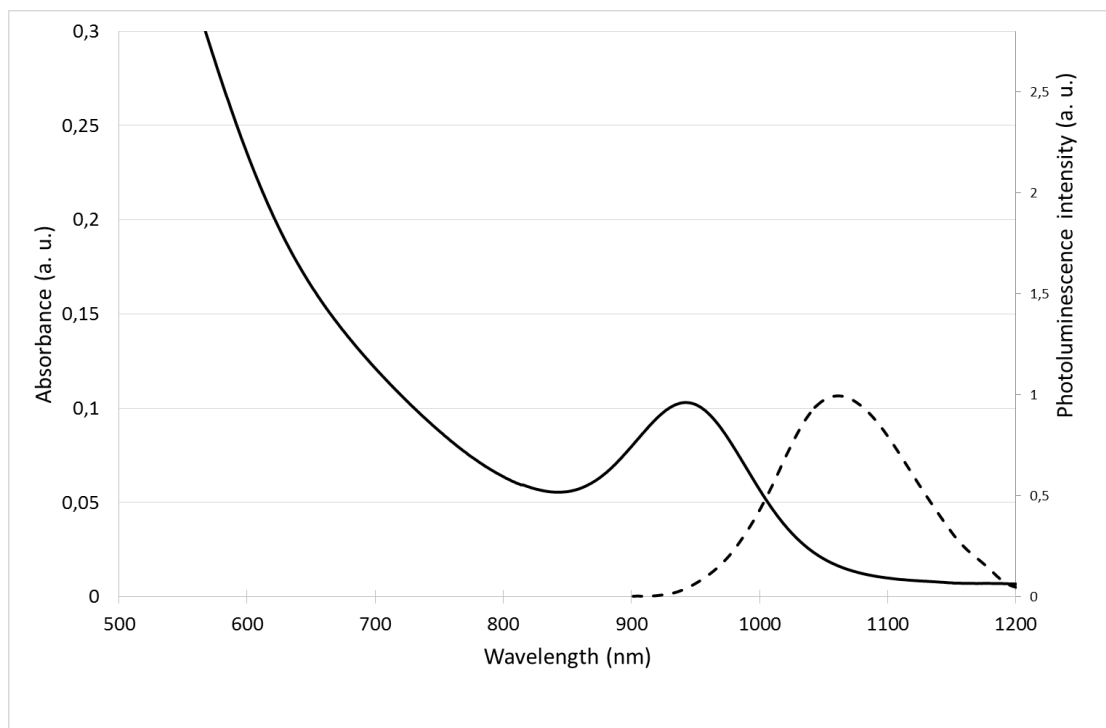


Figure S1. Absorption (straight line) and photoluminescence (dashed line) spectra of the PbS-TBAI QDs recorded in toluene solution. The sample was excited at 700 nm.

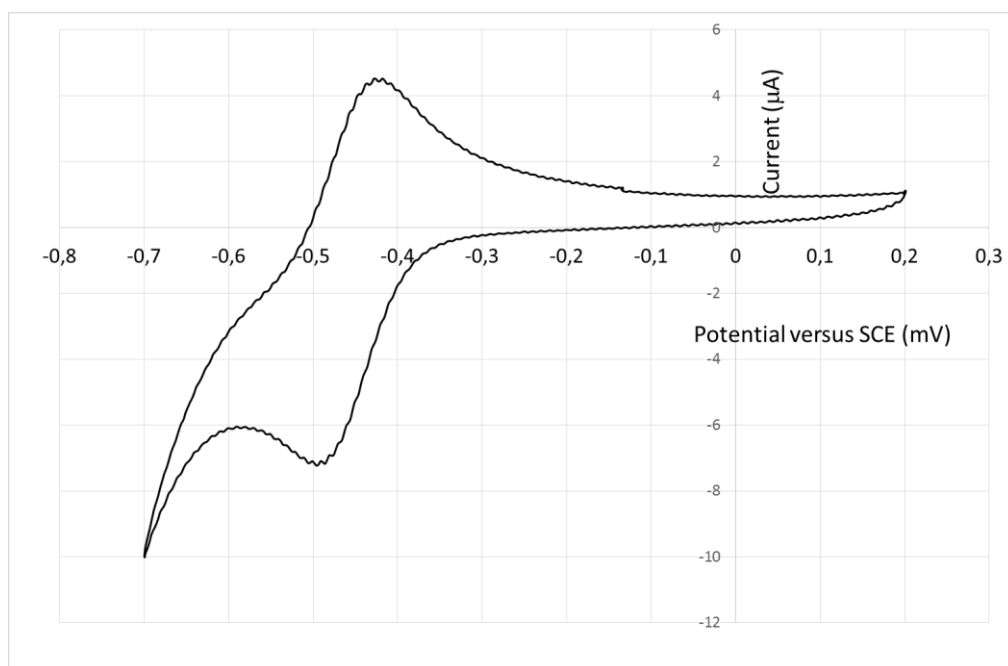


Figure S2. Cyclic voltammogram of py-NDI recorded in CH_3CN with Bu_4NClO_4 as supporting electrolyte (0.1 M), rate 100 mV/sec.

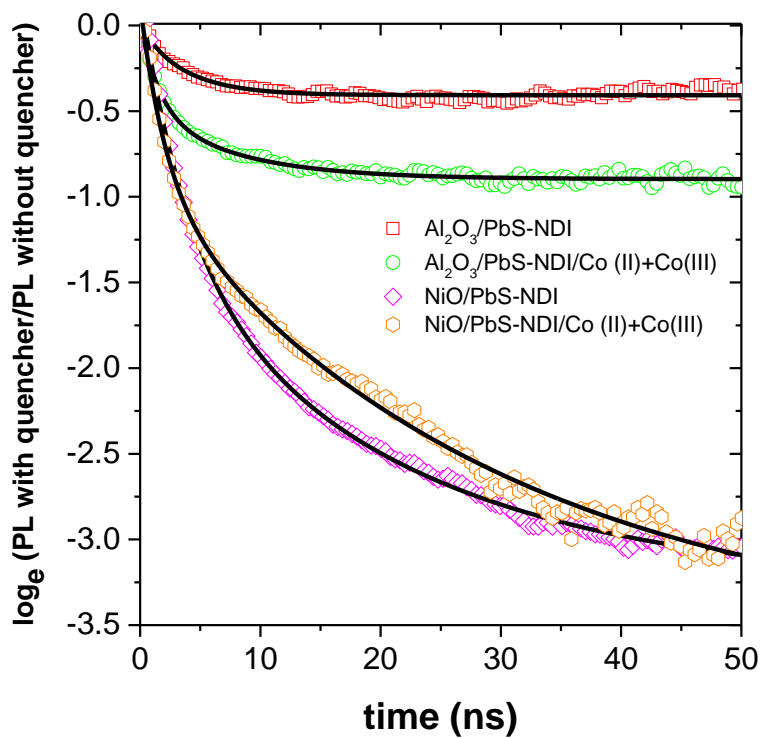


Figure S3. Ratio of photoluminescence kinetics of the 3.0 nm PbS QDs with quencher (electron/hole acceptor) to photoluminescence kinetics without quencher (i.e on alumina). The solid black lines are fits to PL decays

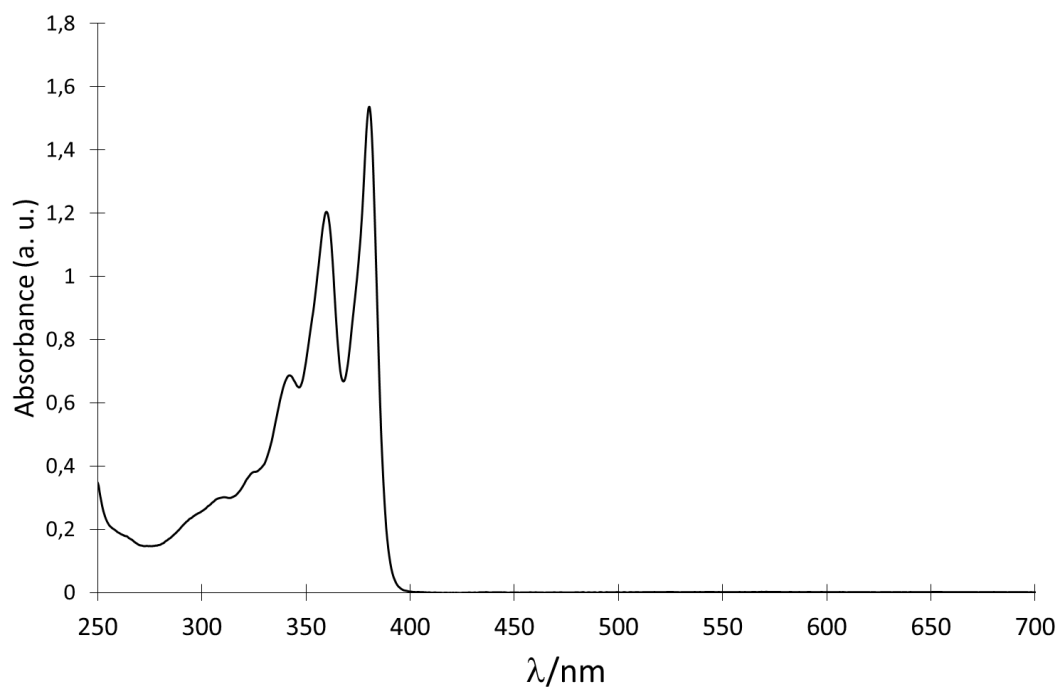


Figure S4. Absorption spectrum of py-NDI recorded in dichloromethane solution.

References:

- [1] M. J. Fuller, M. R. Wasielewski, Photorefractivity in Nematic Liquid Crystals Using a Donor–Acceptor Dyad with a Low-Lying Excited Singlet State for Charge Generation. *J. Phys. Chem. B* 105 (2001) 7216-7219.
- [2] Mahfoudh Raissi, M. T. Sajjad, Y. Pellegrin, T. Roland, S. Jobic, M. Boujtita, A. Ruseckas, I. D. W. Samuel, F. Odobel, Size dependence of efficiency of PbS quantum dots in NiO-based dye sensitised solar cells and mechanistic charge transfer investigation. *Nanoscale* (2017).
- [3] M. Raissi, Y. Pellegrin, S. Jobic, M. Boujtita, F. Odobel, Infra-red photoresponse of mesoscopic NiO-based solar cells sensitized with PbS quantum dot. *Sci. Rep.* 6 (2016) doi: 10.1038/srep24908.