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Synthesis and properties of new benzothiadiazolebased push-pull dyes for p-type dye sensitized solar cells

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Abstract

We report the synthesis of three new push-pull dyes specially designed for the sensitization of mesoporous p type semi-conductor NiO for the construction of p type dye sensitized solar cells (pDSC). Their structure stems from the conjugation of the well-known tris(carboxy-arlyamine) anchoring moiety to a benzothiadiazole acceptor through a fluorene (**PP1**) or thiophene-fluorene linker (**PP2**). Appending a NDI secondary acceptor onto **PP2** yielded a dyad (**PP2-NDI**). The push-pull structure is here particularly adapted to the sensitization of p-

type semi-conducting materials. All three dyes were investigated by spectroscopic and electrochemical techniques, and their electronic properties were modelled by TD-DFT. In all cases, the new sensitizers exhibit adequate absorption features (spanning from 400 nm to 600 nm, extinction coefficients between 20000 and 27000 M⁻¹.cm⁻¹) and their thermodynamic parameters are all in favor of efficient interfacial charge transfers involving NiO. pDSC were constructed with all three dyes; high photoconversion efficiencies (PCE) were reached, especially in the case of dyad **PP2-NDI** (Jsc = 5.90 mA/cm², Voc = 143 mV, FF = 33.8%, PCE = 0.29%), due to a combination of outstanding electronic properties and increased charge separation state lifetime. Tandem DSC (tDSC) composed of a TiO₂ photoanode sensitized by the dye **D35** and a NiO photocathode sensitized by **PP2-NDI** were assembled with two different electrolytes (I₃⁻/T or T₂/T⁻ based electrolytes). The latter gave PCE among the best ever reported for tDSC (Jsc = 5.90 mA/cm²; Voc = 896 mV; FF = 63%, PCE = 2.80% in the case of the I₃⁻/T electrolyte, Jsc = 4.52 mA/cm², Voc = 840 mV, FF = 60% and PCE = 2.27% for T₂/T based devices) unraveling the significance of the new dyes presented in this study.

Keywords: push pull dyes; benzothiadiazole; fluorene linker; dyad; dye sensitized solar cells; tandem cells

1. Introduction

The conversion of solar light into a usable form of energy is one of the greatest challenges ever tackled by the scientific community.¹ Renewable, free and rather well distributed over the globe, sunlight, if mastered, would doubtlessly put an end to the hegemony of fossil fuels and the related energy crisis. Photovoltaic devices are certainly the most advanced artificial systems able to directly convert light into electricity.² Among them, dye sensitized solar cells (DSC) are particularly appealing devices owing to their stability, high efficiency, their aesthetic features and their short payback time, much smaller than the commercialized silicon based devices.³ The latter are even inferior to DSC in many regards, such as flexibility, transparency and increased efficiency in low light conditions.⁴ Classical DSC are based on the sensitization of a wide band gap n type semi-conductor, usually mesoporous TiO₂, by a dye exhibiting adequate electronic properties.^{3,5,6} Upon light soaking, the dye injects electrons in

the conduction band of TiO₂ while a redox mediator regenerates the photo-oxidized chromophore. Since they were brought to center stage by Grätzel and O'Regan in 1991.⁷ an impressive progression of the photoconversion efficiencies (PCE) has been experienced, from 7% to ca. 14% today.⁸ Since year 2000, a new kind of DSC has emerged based on the sensitization of a mesoporous p-type semi-conductor (such as NiO).⁹⁻¹² Those p-type dye sensitized solar cells (pDSC) are based on the injection of holes from a photo-excited dye into the valence band of the semi-conducting material. Importantly, pDSC and nDSC can be associated together to design a tandem dye sensitized solar cell (tDSC) featuring theoretical efficiencies above the Schockley-Queisser limit.^{13,14} Previous works have shown in particular that tDSC exhibit larger photovoltages, independent of the redox mediator.^{12,15-19} High photocurrents are attainable too if care is taken to use different dyes for each semi-conductor, exhibiting complementary absorption spectra in order to avoid screening of light by one dye or the other.^{13,18} The mandatory step for constructing an efficient tDSC is that parent nDSC and pDSC are both efficient and very importantly that both short circuit currents are matched. While impressive photoconversion efficiencies (PCE) have been obtained for nDSC, pDSC still lag behind because of the built-in weaknesses of NiO (color, low conductivity) and counterproductive phenomena such as geminate and interfacial charge recombinations.²⁰⁻²³

Significant work today is devoted to improving the PCE of pDSC, by fishing out a better semi-conducting material than NiO,²⁴⁻³¹ determining new efficient redox mediators,^{17,25,32-36} or synthesizing new efficient dyes.³⁶⁻⁵⁰ The latter obviously play a major part in the overall mechanism of a working pDSC. Within this realm, push pull dyes have early shown their qualities as sensitizers for pDSC.^{44,45,51-57} They exhibit a strongly allowed donor to acceptor transition affording huge extinction coefficients; besides their color can be tuned by modifying the nature of the donor and acceptor groups. Additionally, if the anchor is tethered to the donor side, the hole injection is properly vectorialized, i.e. the very structure of a push pull sensitizer supports hole injection. The localization of the HOMO close to the semiconductor's surface and of the LUMO as far as possible from the latter is a real advantage of injection retard geminate push-pull sensitizers to favor hole and charge recombination.^{14,44,50,52,56,58} Push pull dyes are epitomized by the **P1** dye (chart 1),⁴⁴ the only dye for pDSC which is commercially available. Other push pull dyes have since been isolated, some displaying greater PCE than **P1**.^{18,46,47,59}

Herein we present our own contribution in this field, presenting two new push pull dyes **PP1** and **PP2** (chart 1) based on the association of the well-known trisarylamine anchor (TPA)^{60,61} and the benzothiadiazole acceptor (BTD).^{53,62,63} TPA has been widely used as anchoring group in many dyes for pDSC because it favors hole injection thanks to its electron-rich character. Besides, the presence of two COOH anchors provides additional stability to the dye monolayer.55,58 Regarding the acceptor fragment, BTD shows excellent properties that materialized into a collection of successful opto-electronic devices,⁶²⁻⁶⁵ including sensitizers for pDSC.⁵³ In particular BTD exhibits a reversible reduction potential of ca. -1.2 V vs. SCE, providing sufficient driving force for regeneration of the photo-reduced dye by a great many redox mediators. In the case of **PP1**, the TPA donor is linked to the BTD acceptor by a fluorene spacer which is known to favor the electronic communication between the two ends.^{66,67} Moreover, the presence of 2-ethylhexyl chains on the fluorene moiety provides solubility to the dyes and could passivate the surface of the semi-conductor by preventing the redox mediator from approaching too close and curbing therefore the interfacial charge recombination. In the case of **PP2**, a thiophene moiety is inserted between the BTD and fluorene fragments; increasing the distance and conjugation between donor and acceptor sides entails a rise of the dipole and thus an increase of the extinction coefficient while shifting the transition to the red, both appreciable features for a performant sensitizer. Moreover, the probability of geminate charge recombination decreases as the acceptor (where the electron density is localized after hole injection) is farther away from the semi-conductor's surface.^{40,50}



Chart 1. Structures of P1 and of the dyes investigated in this work.

In order to further curb down the extent of geminate charge recombination, a secondary electron acceptor (naphthalene diimide, NDI) was affixed to **PP2** to yield **PP2-NDI**. Within such a dyad, a secondary "dark" electron transfer from the photo-reduced chromophore onto the secondary acceptor shifts the electron farther away from the semi-conducting material resulting in longer lived charge separation states by several orders of magnitude.^{37,38,68,69}

The syntheses, electronic properties of those three new dyes are disclosed in this contribution, as well as the photovoltaic performances of associated p-type photovoltaic devices. We found that the push-pull nature of the dyes entailed the presence of an intense charge transfer transition in the visible domain, assisting besides the hole injection in the valence band of NiO; appending a secondary acceptor to the best performing push-pull dye afforded the highest PCE in the series because of an improved photo-induced interfacial charge separated state lifetime.

2. Results and discussion

2.1. Synthesis of the dyes

The synthesis of the three new sensitizers **PP1**, **PP2 and PP2-NDI** stems from building block **3** and a stannylated compound derivatized from benzothiadiazole (**6** or **9**) (Schemes 1-2). **PP2-NDI** was synthesized from compound **11**, which is an intermediate of the synthesis of **PP2** (Scheme 3). Compound **3** was obtained from the commercially available building blocks **1** and **2** (Scheme 1), *via* a Buchwald-Hartwig cross-coupling reaction using Pd(dba)₂ as precatalyst and XPhos as ligand. The fluorene derivative **1** was introduced in excess to promote the monocoupling reaction and the desired compound **3** was isolated with a yield of 32% (based on the limiting amine reagent **2**) (Scheme 1). Despite the excess of fluorene derivative, the biscoupling product was isolated with a yield of 58%.



Scheme 1. Synthesis of compound 3. Reagents and conditions: a) Pd(dba)₂, XPhos, t-BuOK, toluene, 100°C, 20h, 32%.

The two stannylated reactants **6** and **9** were obtained from the reaction between the brominated derivatives **5** and **8**, and hexamethyldistannane by a similar catalytic way using $Pd(PPh_3)_4$ as catalyst in DME or toluene, respectively (Scheme 2). It should be noted that compound **9** was purified on triethylamine-neutralized silica gel to avoid hydrolysis of the stannane.



Scheme 2. Synthesis of compounds 8 and 9. Reagents and conditions: a) Pd(PPh₃)₂Cl₂, THF, 80°C, 24h, 20% for compound 5, 80% for compound 7 b) Pd(PPh₃)₄, Sn₂Me₆, DME, 85°C, 24h, 66% c) NBS, CH₂Cl₂, RT, 16h, 32% d) Pd(PPh₃)₄, Sn₂Me₆, toluene, 100°C, 5h, 86%.

A Stille coupling between building block **3** and stannylated derivatives **6** or **9** afforded respectively compound **10** and **11** in about 50% yield (Scheme 3). For compound **11**, the classical Stille conditions (Pd(PPh₃)₄ in toluene at 100°C) gave a satisfactory yield. However, they were not well adapted to synthesize compound **10**, probably due to the steric hindrance generated by the benzothiadiazole moiety on the ortho position of the stannylated compound **6**. Mee et al. have studied the reactivity for Stille reaction of some less reactive arylstannanes,⁷⁰ and they discovered a synergic catalytic system using CuI in combination with CsF, affording good results in difficult cases. We have used these conditions to realize the coupling between **3** and **6** yielding compound **10** with a yield of 53%.



Scheme 3. Synthesis of dyes **PP1** and **PP2**. Reagents and conditions: a) PdCl₂, P(t-Bu)₃, CuI, CsF, DMF, 50°C, 18h, 53% b) TFA, CH₂Cl₂, RT, 4-5h, 99% c) Pd(PPh₃)₄, toluene, 110°C, 24h, 69%.

The hydrolysis of the *tert* butanol ester groups was realized by action of TFA in dicholoromethane and allowed isolating the sensitizers **PP1** and **PP2** in high yields as yellow and red powders, respectively.

The synthesis of **PP2-NDI** was accomplished in three steps from the intermediate compound **11**. The first step is a selective iodination reaction, already used for other thiophene derivatives^{71,72} and afforded **12** in 84% of yield. Sonogashira cross-coupling reaction between **12** and ethynyl NDI **13** afforded the dyad **PP2-NDI** after hydrolysis of the *tert* butanol ester groups of **14** with TFA.



Scheme 4. Synthesis of dyes PP2-NDI. Reagents and conditions: a) $Hg(OCp)_2$, CHCl₃/AcOH, 1h, RT and then I₂, 3h, RT, 84% over two steps; b) TFA, CH₂Cl₂, RT, 4-5h, 99%; c) Pd(PPh₃)₄, toluene, 110°C, 24h, 69%. c) TFA, CH₂Cl₂, RT, 5h, 96%.

2.2. Electronic UV-visible absorption and emission spectroscopy

The absorption and emission spectra of all dyes were recorded in dichloromethane solution at room temperature (Figure 1). The optical data including wavelengths of maximal absorption (λ_{abs}) with extinction coefficient (ϵ), wavelength of maximal emission (λ_{em}) and 0-0 energy level of the lowest singlet excited state (E₀₀), are collected in Table 1.

The UV-Visible absorption spectra of **PP1** and **PP2** in dichloromethane exhibit an intense absorption band in the visible, respectively at 438 and 485 nm attributed to a π - π * transition with a moderate charge transfer character (see calculations below) with molar extinction coefficient (ϵ) values of ca. 20 000 and 27 000 M⁻¹.cm⁻¹ at λ_{max} . It should be noted that the extension of the π -conjugated system with a thiophene unit (from **PP1** to **PP2**) induces a large bathochromic shift of around 50 nm and an increase of the molar extinction coefficient. These properties enable enhancing the ability of **PP2** to harvest sunlight compared with **PP1**. Both dyes show another absorption band around 350-380 nm with a molar extinction coefficient of

around 50000 M⁻¹.cm⁻¹. The theoretical results show this band is a π - π * transition globally delocalized on the whole dye, with a limited charge transfer.



Figure 1. Electronic absorption (straight line) and normalized steady state emission (dashed lines) spectra of the sensitizers **PP1**, **PP2** and **PP2-NDI** recorded in dichloromethane solution.

PP2 and **PP2-NDI** exhibit a similar absorption spectra. The main change consists in the appearance of two narrow bands at 361 and 380 nm on the spectrum of **PP2-NDI**, which can be attributed, after analyzing the theoretical spectrum obtained with quantum calculations, to the contribution of NDI localized absorption features, mixed with the bands in the UV described above for **PP1** and **PP2**. For this reason, that band reaches a global molar extinction coefficient of around 80000 M^{-1} .cm⁻¹. More importantly, the main absorption band in the visible is significantly broader and slightly red-shifted compared to **PP2**. Accordingly, the NDI unit is electronically decoupled from the rest of the molecule because of a well-known orbital node on the nitrogen atom of the diimide group.⁷³ It is thus unlikely that the NDI be responsible for the broader and bathochromically shifted absorption band of **PP2-NDI** vs. **PP2**. However, the phenylacetylene spacer formally bridging **PP2** to the NDI moiety in the dyad extends the conjugation of the π system and account for the differences observed between **PP2-NDI** and **PP2**. This red-shift is actually validated by our quantum calculations, returning a LUMO+1 energy level for **PP2-NDI** lower than the LUMO of plain **PP2** (by 0.13 eV), while their respective HOMO levels remain unchanged.

PP1 and **PP2** are both fluorescent at room temperature in diluted dichloromethane solutions when excited at λ_{max} and show an emission band with maxima at 596 and 621 nm, respectively (Figure 1). Unsurprisingly, λ_{em} and λ_{abs} follow the same trend for **PP1** and **PP2**. The Stokes shifts are rather large (respectively 6051 and 4516 cm⁻¹, table 1) indicating a significant redistribution of the electron density upon excitation and supporting the assumption that the absorption band in the visible possesses a significant charge transfer character. The addition of the NDI unit almost completely quenches the fluorescence. By analogy to other work on related dyads, we could hypothesize that the singlet-excited state is quenched by photoinduced electron transfer to form ⁺**PP2-NDI**.^{37,49,50,74}

Table 1. Wavelengths of maximal absorption (λ_{abs}) with extinction coefficient (ε) , wavelength of maximal emission (λ_{em}) recorded at room temperature in dichloromethane, associated Stokes shift and zero-zero energy level of the lowest singlet excited state (E_{00}) .

Dyes	λ_{abs} /nm (ϵ /M ⁻¹ cm ⁻¹)	λ_{em} /nm	Stokes shift / cm ⁻¹	^a E ₀₀ / eV
PP1	438 (20000); 352 (46600)	596	6051	2.41
PP2	485 (27100); 364 (61200)	621	4516	2.23
PP2-NDI	502 (26400) 380 (77500); 361 (81300)	651	4560	2.15

^acalculated according to the equation: $E_{00} = 1240/\lambda_{inter}$, with λ_{inter} being the wavelength at the intersection of the normalized absorption and emission spectra.

2.3. Electrochemical study and electron transfer driving forces

The three new sensitizers were studied by cyclic voltammetry (Table 2) to determine their redox potentials and estimate the hole injection (ΔG°_{inj}) and dye regeneration (ΔG°_{reg}) driving forces (Table 2).

For each dye, an oxidation process occurs around 1.0 V *vs.* SCE with a generally non-reversible or weakly reversible wave attributed to the arylamine moiety.^{16,68} The HOMO level seems to be weakly influenced by the introduction of the thiophene unit between the fluorene connecting group and the BTD acceptor (0.05 V shift between **PP1** and **PP2**). A similar shift though of larger amplitude (0.17 eV) was obtained when examining the DFT-computed

HOMO energy levels. **PP1** and **PP2** are respectively reversibly reduced at -1.4 and -1.3 V vs. SCE. The comparison of these values indicates the stabilization of the LUMO level of PP2 compared to PP1, in agreement with the red-shifted band of PP2 observed on the absorption spectra. This is also the case when considering the **PP1** and **PP2** LUMO theoretical levels obtained with our quantum scheme, located respectively at -1.80 and -1.96 eV. For the sensitizer **PP2-NDI**, the two first reversible reduction processes take place on the NDI moiety around -0.6 and -1.0 V vs. SCE. Unsurprisingly, the DFT LUMO localized on the NDI (see below) is also shifted to lower energy (-2.63 eV) compared to its PP1 and PP2 counterparts. Using both electrochemical and spectroscopic data, we estimated the Gibbs free energies for the various charge transfer processes. It can be noted that the hole injection process into NiO valence band for each sensitizer display sufficient exergonicity (superior to 500 meV, Table 2). Besides, **PP1** and **PP2** feature very large regeneration driving forces with common redox mediators (ca. 1 eV for iodine based electrolytes, more than 1.5 eV for disulfide/sulfide based redox mediators). When appending NDI to PP2, a severe drop of the photo-reduced dye regeneration is naturally experienced, given that hole injection should be followed by a quick electron shift from the PP2 moiety to the NDI unit. The loss in regeneration driving force is usually counter-balanced by an important rise of the interfacial charge separation state lifetime, a beneficial feature when the regeneration process is sluggish. As reported in previous work, geminate charge recombination (i.e. between holes in NiO and the photoreduced sensitizer) is indeed a very deleterious process (among others), which prevents pDSC reaching high output performances comparable to conventional nDSC.^{38,75-77} Grafting secondary acceptors on efficient dyes proved to be a very powerful method to decrease geminate charge recombination, at the expense though of the regeneration driving force.^{37,49,50,74}

Given the estimation of the driving forces for the various charge transfer processes dyes **PP1**, **PP2** and **PP2-NDI** should be efficient sensitizers for pDSC.

Table 2. Redox potentials recorded by cyclic voltammetry at room temperature in dichloromethane/DMF [95:5] solution with Bu_4NPF_6 (0.1 M) as supported electrolyte and referenced *versus* saturated calomel electrode (SCE). Calculated Gibbs free energies for hole injection (ΔG°_{inj}) and dye regeneration (ΔG°_{reg})

Dyes	$\frac{E (S^{+}/S) (V)}{\Delta E (mV)}$	$E_{1/2} (S/S^{-}) (V)$ $\Delta E (mV)$	E _{1/2} (NDI/NDΓ) (V) ΔE (mV)	^a E (S*/S ⁻) (V)	^b ΔG° _{inj} (eV)	$^{c}\Delta G^{\circ}_{reg}$ with I_{3}^{-} (eV)	$^{d}\Delta G^{\circ}_{reg}$ with T_{2}/T^{-} (eV)
PP1	1.01 (90)	-1.40 (110)	-	1.01	-0.71	-1.08	-1.65
PP2	0.95 (70)	-1.29 (80)	-	0.94	-0.64	-0.97	-1.54
PP2-NDI	1.04 ^e	-1.20 (100)	-0.59 (90)	0.95	-0.65	-0.27	-0.88

^aCalculated according to the equation: $E_{1/2}(S^*/S^-) = E_{1/2}(S/S^-) + E_{00}$. ^bCalculated according to the equation: $\Delta G^{\circ}_{inj} = E_{BV}(NiO)$ - $E_{Red}(S^*/S^-)$ with $E_{BV}(NiO) = 0.30$ V vs. SCE. ^cCalculated according to the equation: $\Delta G_{reg} = E_{Red}(S/S^-) - E(I_3^-/I_2^{-\bullet})$ with $E(I_3^-/I_2^{-\bullet}) = -0.32$ V vs. SCE. ^dCalculated according to the equation: $\Delta G_{reg} = E_{Red}(S/S^-) - E(T_2/T^-)$ with $E(T_2/T^-) = 0.25$ V vs. SCE. ^eNon reversible process, peak potential.

2.4. Quantum chemical calculations

TD-DFT calculations were undertaken in order to have a deeper understanding of the optical and electrochemical properties of dyes **PP1**, **PP2** and **PP2-NDI**. The key results are gathered in Table 3. The frontier orbitals of interest are represented in Figure 2. The HOMO and HOMO-1 are delocalized over the whole push-pull structure and importantly on the anchoring triphenylamine moiety, which is favorable for hole injection in the valence band of NiO.²² Conversely, the LUMOs are centered on the benthiadiazole acceptor end of the dyes **PP1** and **PP2**, thus shifting the electron density away from the semi-conductor surface and limiting geminate charge recombination. In **PP2-NDI**, the LUMO is purely centered on the NDI moiety as expected for this kind of dyad-dye,^{38,50,78} which corroborates the electrochemical measurements. The calculated absorption spectra reproduce quite well the experimental data, the computed λ_{abs} values following the experimental ranking. The transitions are similar for the three dyes, mainly HOMO and HOMO-1 to LUMO for **PP1** and **PP2**, and HOMO and

HOMO-1 to LUMO + 1 for **PP2-NDI** since the LUMO is localized on the NDI in this case; the latter is completely isolated from the rest of the molecule from the point of view of the electronic communication and therefore does not participate in the intense transition in the visible due to a poor overlap with the occupied orbitals. Ground and excited state dipole moments indicate incidentally that the structures for **PP1** and **PP2** are adequately designed to favor photo-induced hole transfer into NiO.¹⁴ Interestingly, the computed transferred charge q^{CT} upon visible light irradiation is almost constant for the three dyes but the charge transfer distance d^{CT} is substantially higher for **PP2** than **PP1** or **PP2-NDI**, a promising feature for an efficient photo-induced hole injection into NiO. To sum up, the computed structures respect the requested features in the design of efficient dyes for pDSC.

At this point, changes in the hole injection process between the three dyes can be intuited and directly related to photovoltaic efficiency. In particular the impact of the NDI unit can be clearly highlighted. First, we note that the ground and excited state dipole moments values indicate that the structures for PP1 and PP2, and PP2-NDI are adequately designed to favor photo-induced hole transfer into NiO,¹⁴ and, that, the highest excited state dipole moment is obtained for **PP2**. The computed transferred charge q^{CT} upon visible light irradiation is almost constant for the three dyes but the charge transfer distance d^{CT} is again substantially higher for PP2 than PP1 or PP2-NDI. Thus PP2 dye is expected to yield the most efficient hole creation after vertical excitation among the series, and the presence of the NDI unit is not modifying this "FC" picture. However, when considering the presence of a NDI-localized LUMO in PP2-NDI (Figure 2), one can expect, as evoked earlier, that the electron will be transferred to this secondary acceptor unit where it will be trapped, away from the benthiadiazole (LUMO+1). This yields to an improved separation of the electron/hole pair and, consequently, an important drop in the charge recombination. Assuming fast electron transfer, PP2-NDI should therefore outperform both PP1 and PP2. To sum up, all the computed structures respect the requested features in the design of efficient dyes for pDSC. Yet, both quantitative and mechanistic discrepancies are highlighted for the hole injection and charge recombination process within the series, that are further clarified with the photovoltaic measurements.

Table 3. Computed Wavelength of Maximal Absorption (λ abs) with Oscillator Strengths (f), Ground-state and (first) Excited-state Dipole Moment (μ), Charge-Transfer Distance (d^{CT}), and Amount of Transferred Charge (q^{CT})

Dye	λ_{abs} / nm (f/au)	$\mu/{ m D}$	$d^{ ext{CT}}/ ext{\AA}$	$q^{ ext{CT}}$ /e
PP1	422 (0.87)	1.19/4.61	1.50	0.60
PP2	474 (1.12)	0.30/6.44	2.42	0.58
PP2-NDI	501 (1.67)	0.87/5.01	1.73	0.57

Figure 2. a) Frontier molecular orbitals (isovalue: 0.02 au) and b) transition densities of the first excited-state (isovalue: 0.0004 au) for the different dyes. Green (white) areas correspond to a gain (loss) of electronic density.

3. Photovoltaic measurements

As mentioned above, all new dyes presented in this study are able to thermodynamically inject holes in the valence band of NiO. pDSC were thus prepared in order to evaluate the performances of PP1, PP2 and PP2-NDI in NiO based hybrid photovoltaic devices, using three different electrolyte compositions. All details concerning the preparation of the cells are gathered in the experimental section. Briefly, optimized mesoporous 3.5 µm thick NiO electrodes were prepared by screen printing a home-made NiO ink on FTO substrates. Importantly, a dense layer of NiO was carefully deposited on the FTO substrates in order to improve the ohmic contact between FTO and NiO.⁷⁹ The as-obtained electrodes were sintered at 400°C for 30 minutes and a last nickel acetate treatment was performed on the NiO electrodes in order to passivate the superficial defects.^{80,81} The electrodes were dipped in the dye solution overnight, then washed and dried. They were finally assembled with a platinum coated FTO substrate using a 25 µm hotmelt spacer and an electrolyte was introduced by vacuum back-filling. The performances of the pDSCs recorded under AM1.5 simulated solar light are gathered in Table 4 for the different electrolytes, and the corresponding J/V curves are given in figure S1. Among the three dyes, PP2-NDI undeniably yields much better photoconversion efficiencies than PP1 and PP2 due to enhanced Voc and particularly high Jsc. The latter is illustrated by the higher external quantum efficiency (EQE) spectra obtained for PP2-NDI (Figure 3). Cells prepared with PP1 and PP2 feature similar performances, PP2 being nevertheless substantially better than PP1, consistently with abinitio calculations, owing to a higher short circuit current density (Jsc, 25% better for PP2 based device in the case of the iodine based electrolyte). The latter parameter is given by the following formula:

$Jsc = \eta_{coll} x \eta_{inj} x \eta_{reg} x LHE$

where η_{coll} , η_{inj} , η_{reg} are respectively the charge collection, injection and regeneration quantum yields and LHE is the light harvesting efficiency. Given the thermodynamic parameters involved for **PP1** and **PP2** (Table 2), one can fairly consider that η_{coll} , η_{inj} and η_{reg} are similar for both **PP1** and **PP2** based photocathodes. However, **PP2** is endowed with a higher extinction coefficient than **PP1** and red-shifted absorption bands leading to an enhanced light harvesting efficiency (LHE) for the **PP2**|NiO photocathode, most likely accounting for the improved Jsc. The larger charge transfer distance for **PP2** (computational chemistry section, Table 3) is an appreciable factor too to explain the better efficiency of the latter dye than **PP1**.

As mentioned above, the best dye in the series is by far **PP2-NDI**, mostly because of an impressive average Jsc of 5.90 mA/cm² and a large Voc of 143 mV. Although **PP2-NDI**

displays slightly better optical properties than **PP2**, those cannot account for the blatant improvement of the photocurrent, nor could a better η_{inj} since injection driving forces are similar for both dyes. Incidentally, dyad **PP2-NDI** features the weakest regeneration driving force because of the appended NDI acceptor moiety (Table 2). As intuited from the quantum calculations, after the photo-induced hole injection, a quick electron shift is expected to occur from the PP2 fragment to the NDI secondary acceptor as observed before in dyadic sensitizers.^{37,49,50,74} This charge shift allows an increase in the interfacial charge separation state at the expense of the regeneration driving force, which is here around 700 meV smaller for **PP2-NDI** than **PP1** or **PP2**. Given the obtained performances, such a sacrifice was a necessary evil: the increased lifetime of the charge separated state NiO⁽⁺⁾|**PP2-NDI**⁽⁻⁾ is synonymous with a dramatically curbed geminate charge recombination.^{38,50,78} η_{coll} is therefore much improved explaining the higher Jsc, as well as the significantly increased Voc for **PP2-NDI** devices compared to **PP1** and **PP2** ones.

Iodine based electrolytes are not optimal for DSC in general and NiO based pDSC in particular. I_3^- is indeed corrosive (limiting the lifetime of the DSC), quite intensely colored (partly screening the dyes from solar light), $E(I_3/\Gamma)$ is too positive limiting the attainable Voc and the Γ to I_3^- oxidation reaction is catalyzed by NiO (increasing the extent of the interfacial charge recombination). Cobalt and iron complexes proved to be interesting alternatives.³²⁻³⁵ Within this frame, we tested the $Co1^{3+}/Co1^{2+}$ based electrolyte (where $Co1^{n+}$ is the tris(4.4'diterbutyl-2,2'-bipyridine)cobalt⁽ⁿ⁺⁾ complex, cf. Figure S3 for the structures of the compounds) with the three new dyes. Importantly, this redox mediator is only compatible with a photocathode where the interfacial charge separation state $NiO^{(+)}|Dye^{(-)}$ is long lived.^{35,37} Cells elaborated with dyes **PP1** and **PP2** thus performed poorly with this electrolyte because of an assumed very fast geminate charge recombination. On the other hand, pDSCs built with dyad **PP2-NDI** featured a respectable Jsc of 1.72 mA/cm² (Table 4), in accordance with a rather efficient dye regeneration by $Co1^{3+}$. In this case, a remarkable Voc of ca. 340 mV was obtained agreeing with previously published work.^{38,50,78} The improved output potential is assigned to the severely decreased interfacial charge recombination between holes in the valence band of NiO and the negative charges borne by the very bulky $Co1^{2+}$.^{35,37,82} This result is additional evidence that the interfacial photo-induced charge separated state is long lived, and therefore that the "dark" electron shift from the PP2 moiety to the NDI unit is efficient.

In 2010, redox mediators based on a tetrazole-thiolate and its disulfide dimer (T_2/T^- couple) (Figure S3) "rivaled" the I_3^-/T couple within a classical Grätzel cell.⁸³ Shortly after that, the T_2/T^- couple was successfully tested in pDSCs, showing great promise towards improved Voc because of decreased interfacial charge recombination processes and a 70 mV less positive potential $E(T_2/T^-)$.^{17,25} Additionally, the T_2/T^- electrolyte is almost colorless allowing more light to be collected by the sensitizer. **PP1**, **PP2** and **PP2-NDI** were therefore tested with the latter and the same trends than above were monitored, with **PP1** and **PP2** lagging well behind **PP2-NDI**, likely for the same reasons as those applying to iodine and cobalt based electrolytes (e. g. fast geminate charge recombination). Interestingly, Voc were raised in all cases (by 55, 42 and 69 mV for **PP1**, **PP2** and **PP2-NDI** based pDSC respectively) as previously observed.¹⁷ This can be assigned to the less positive redox potential of T_2/T^- , but a quick examination of the J/V curves recorded in the dark revealed that the dark current substantially decreased too with T_2/T^- compared to I_3^-/T (Figure S2).

Table 4. Mean Photoelectrochemical Metrics of the p-DSCs sensitized with **PP1**, **PP2** and **PP2-NDI** dyes and employing either the triiodide/iodide (I_3^-/Γ), disulfide/sulfide (T_2/T^-) or cobalt (**Co1**³⁺/**Co1**²⁺) electrolytes recorded under AM1.5 G Simulated Sunlight (1000 W/m²).

Dye	Electrolyte	Jsc (mA/cm ²)	Voc (mV)	FF (%)	η (%)
PP1	I_3/I	1.53 ± 0.03	113.6 ± 3.3	31.9 ± 0.4	0.055 ± 10^{-4}
	T_2/T^-	1.60 ± 0.09	168.9 ± 7.8	30.5 ± 0.7	0.082 ± 0.002
PP2	I ₃ ⁻ / I ⁻	2.15 ± 0.05	115.6 ± 5.4	30.6 ± 0.7	0.075 ± 10^{-4}
	T_2/T^{-1}	1.82 ± 0.03	157.5 ± 0.8	31.5 ± 0.1	0.090 ± 0.001
PP2-NDI	I ₃ ⁻ /I ⁻	5.90 ± 0.01	143.1 ± 2.5	33.8 ± 0.3	0.29 ± 0.005
	T_2/T^{-1}	4.31 ± 0.19	212.5 ± 7.8	33.9 ± 0.5	0.23 ± 0.01
	Co ^{III} /Co ^{II}	1.72 ± 0.01	342.2 ± 11.3	39.7 ± 0.3	0.31 ± 0.01





Figure 3. External quantum efficiencies (EQE) of the dyes in NiO based DSCs.

The interesting performances of **PP2-NDI**, and in particular the high average Jsc obtained with an I₃⁻/ Γ electrolyte based pDSC prompted us to construct tandem cells incorporating a NiO|**PP2-NDI** half-cell such as those presented above. A tandem DSC (tDSC) is based on a photoanode and a photocathode facing each other and bathed in the same electrolyte. The photoanode was made of on a 4 µm thick TiO₂ mesoporous electrode sensitized by well-known orange **D35** push pull dye (cf figure S3). The latter was chosen because of its intense absorption features and its high efficiency and compatibility with various redox mediators.⁸⁴⁻⁸⁶ Besides **D35** is an organic dye like **PP2-NDI**; this is advantageous compared to heavy metal based dyes such as **N719**, from the environmental and financial points of view.

First, the performances of the sub-cells prepared with the T_2/T^- and I_3^-/T^- electrolytes were evaluated under AM 1.5 simulated solar light. Typical J-V curves are given in Figure 4 and all the results are gathered in Table 5.

Table 5. Metrics of the tandem and sub-cells recorded under simulated AM1.5 (100 mW/cm^2) with I_3^{-}/Γ and T_2/T^{-} based electrolytes.

	electrolyte	Jsc (mA/cm ²)	Voc (mV)	FF (%)	η (%)
NiO PP2-NDI	I_3^{-}/I^{-}	6.48	175	34	0.38
	T_2/T^-	4.50	204	34	0.31
TiO ₂ D35	I_3^-/I^-	7.41	764	65	3.72
	T_2/T^-	6.94	641	61	2.6
tDSC	I_3^-/I^-	5.07	896	63	2.80
	T_2/T^-	4.52	840	60	2.27

The EQE of each sub-cell is given in Figure S4 and confirms that the photoanode is able to fill the absorption gap (between 420 and 520 nm) left by the PP2-NDI NiO photocathode. A substantial overlap is nevertheless observed and explains that the tandem cells display a slightly smaller Jsc than each sub-cell taken separately (table 5, figures 4 and S5), regardless of the electrolyte. However, a quite high output potential of almost 900 mV is obtained in the case of the I_3/Γ electrolyte roughly corresponding to the sum of each sub-cell's Voc. A smaller Voc of 840 mV was measured for T_2/T^2 based tDSC (figure S5) mainly because of the smaller photopotential generated by TiO₂|D35 sub-cell as a consequence of higher interfacial charge recombination. Let us lay stress under the fact that D35 based half cells are very performant although only a thin layer of mesoporous TiO₂ was used; the high Voc obtained are particularly beneficial for the elaboration of a tandem cell, justifying again the use of D35 in our case. Nevertheless, the high Jsc and Voc measured with these tandem cells highlight their added value, especially when care is taken to use sensitizers showing complementary absorption spectra and exhibiting high performances in half cells. Overall, an impressive photoconversion efficiency of 2.80% was measured for the TiO₂|D35 / I₃/I / PP2-NDI|NiO tDSC, one of the highest reported so far for tDSC.^{12,16-19,87}



Figure 4. J-V characteristic for the TiO₂|**D35** / I_3^-/Γ / **PP2-NDI**|NiO tDSC (purple lines) and associated half cells (TiO₂|**D35** in yellow and **PP2-NDI**|NiO in red). All cells measured with the same I_3^-/Γ electrolyte. Dotted lines are assigned to dark curves.

4. Conclusion

In this contribution, two new push pull sensitizers **PP1**, **PP2** and the associated dyad **PP2-NDI** were specially designed for pDSC, synthesized and completely characterized by spectroscopic and electrochemical means. The acquired experimental data confirmed that all three dyes show excellent light harvesting abilities between 400 and 600 nm and are capable to inject holes in the valence band of NiO. Significant photovoltaic performances of pDSC fabricated with those new dyes with three very different electrolytes (triiodide/iodide, disulfide/thiolate T₂/T and cobalt based **Co1**³⁺/**Co1**²⁺) were obtained, showing the versatility of the former. The best performances were nevertheless attained with **PP2-NDI** in combination with the I₃⁻/T electrolyte, which prompted us to build tandem cells allowing us to obtain a tDSC which behaved well under irradiation, featuring the expected enhanced Voc of ca. 900 mV and a satisfyingly high Jsc of 5 mA/cm² affording a high PCE of 2.8%, one of the best ever reached by a tDSC. Moreover, both **PP1** and **PP2** feature quite negative reduction potentials, providing sufficient regeneration driving force for a large panel of redox mediators, and a diversity of catalysts for water or CO₂ reduction in order to build dyesensitized photoelectrosynthesis cells.^{88-91,92,93}

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6. Experimental section

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; 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) or to an internal reference (TMS, $\delta = 0$ 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 performed by using a SP300 **Bio-Logic** were 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. UV-visible absorption spectra were recorded on a Variant Cary 300, using 1 cm path length cells. Emission spectra were recorded on a Fluoromax-4 Horiba Jobin Yvon spectrofluorimeter (1 cm quartz cells).

Chemicals were purchased from Sigma-Aldrich or Alfa Aesar and used as received. Thinlayer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735 Kieselgel $60F_{254}$. Column chromatography was carried out either with Merck 5735 Kieselgel 60F(0.040-0.063 mm mesh).

Compounds named di-*tert*-butyl 4,4'-azanediyldibenzoate (**2**),⁹⁴ 4-bromo-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**5**),⁹⁵ 4-(5-bromothiophen-2-yl)-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (**8**)⁹⁶ and ethynyl-NDI (**13**)⁹⁷ were prepared according to already described methods published in the literature.

Compound 3

Compound **2** (670 mg, 0.18 mmol, 1 eq) and 2,7-dibromo-9,9-bis(2-ethylhexyl)-9*H*-fluorene (**1**) (2.0 g, 3.7 mmol, 2 eq) were dissolved in dry toluene (20 mL). The solution was degassed

and potassium *tert*butoxide (310 mg, 2.7 mmol, 1.5 eq), Pd(dba)₂ (40 mg, 0.073 mmol, 0.04 eq), XPhos (70 mg, 0.15 mmol, 0.04 eq) were added. The resulting suspension was degassed and stirred for 20 hours at 100 °C. After completion of the reaction monitored by TLC, the mixture was diluted with dichloromethane and water. The mixture was extracted with dichloromethane (3x) and the organic layer was washed with brine (2x), dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: dichloromethane / petroleum spirit [3/2, v/v]) to give compound **3** (0.49 g, yield of 32%) as a light-yellow oil. ¹H NMR (300 MHz, CDCl₃, 25 °C), δ (ppm): 7.85 (d, J= 8.8 Hz, 4 H), 7.62-7.49 (m, 4 H), 7.11-7.03 (m, 6 H), 1.97-1.73 (m, 4 H), 1.58 (s, 18 H), 1.03-0.40 (m, 30 H). ¹³C NMR (75 MHz, CDCl₃, 25 °C), δ (ppm): 165.4, 152.8, 152.1, 150.7, 145.3, 139.5, 130.7, 130.1, 127.2, 126.1, 125.8, 122.3, 122.2, 122.1, 120.9, 120.8, 120.4, 80.7, 55.3, 44.4, 34.7, 33.4, 28.6, 28.2, 27.3, 26.4, 23.9, 22.9, 22.7, 20.8, 17.5, 14.1, 10.6, 9.9. HRMS (MALDI-TOF) m/z: [M]⁺ calculated for C₅₁H₆₆BrNO₄: 835.4170; found: 835.4141. Δ = 3.5ppm.

Compound 6

Compound **5** (804 mg, 2.70 mmol, 1 eq) and hexamethylditin (2.65 g, 8.1 mmol, 3 eq) were dissolved in dry DME (25 mL). The solution was degassed and the catalyst Pd(PPh₃)₄ (156 mg, 0.13 mmol, 0.05 eq) was added. The resulting mixture was stirred for 48 hours at 90 °C. After completion of the reaction, the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel (eluent: petrol spirit) to give compound **6** (670 mg, yield of 66%) as a yellow solid. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 8.08 (dd, J= 1.1 Hz, J=3.7 Hz, 1 H), 7.77 (d, J= 6.8 Hz, 1 H), 7.72 (d, J= 6.8 Hz, 1 H), 7.43 (dd, J= 5.1 Hz, J= 1.1 Hz, 1 H), 7.20 (dd, J= 3.6 Hz, J= 1.1 Hz, 1 H), 0.46 (s, J_{Sn-H}= 27.4 Hz, J_{Sn-H}= 28.6 Hz, 9 H). ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 161.0, 151.4, 139.7, 137.5, 137.3, 136.9, 127.9, 127.6, 127.2, 126.5, -7.1, -7.2, -8.9, -10.7, -10.7. ¹¹⁹Sn NMR (150 MHz, C₆D₆, 25 °C), δ (ppm): -28.3. HRMS (ESI+) m/z: [M+H]⁺ calculated for C₁₃H₁₅N₂S₂Sn: 378.9689; found: 378.9689. Δ = 0.0 ppm.

Compound 9

In a sealed tube were introduced compound **8** (250 mg, 0.66 mmol, 1 eq) and Pd(PPh₃)₄ (38 mg, 0.033 mmol, 0.05 eq) under argon. Degassed toluene (10 mL) was injected via septum. Hexamethylditin (0.41 mL, 2.0 mmol, 3 eq) was then injected and the mixture was stirred at 100 °C for 6 h. The cooled solution was concentrated under reduced pressure and the crude product was purified by column chromatography on silica gel (eluent: petroleum spirit/triethylamine [90/10, v/v]). The desired compound **9** was obtained as an orange solid with a yield of 86% (264 mg). ¹H NMR (300 MHz, CDCl₃, 25 °C), δ (ppm): 8.18 (d, J= 3.5 Hz, 1 H), 8.10 (dd, J= 3.7 Hz, J= 1.1 Hz, 1 H), 7.84 (s, 2 H), 7.44 (dd, J= 5.1 Hz, J= 1.1 Hz, 1 H), 7.30 (d, J= 3.5 Hz, 1 H), 7.20 (dd, J= 3.7 Hz, J= 5.1 Hz, 1 H), 0.45 (s, J_{Sn-H}= 27.6 Hz, J_{Sn-H}= 28.9 Hz, 9 H). ¹³C NMR (75 MHz, CDCl₃, 25 °C), δ (ppm): 152.6, 145.0, 140.4, 139.5, 136.1, 128.5, 128.0, 127.4, 126.7, 126.1, 125.9, 125.7, -5.6, -5.7, -8.1, -10.5, -10.6. ¹¹⁹Sn NMR (150 MHz, C₆D₆, 25 °C), δ (ppm): -25.3. HRMS (ESI+) m/z; [M+Na]⁺ calculated for C₁₇H₁₆N₂S₃SnNa: 486.9390; found: [M+Na]⁺ 486.9390. Δ =0.7 ppm.

Compound 10

In a Schlenk tube under argon were introduced: compound **3** (50 mg, 0.060 mmol, 1 eq), compound **6** (34 mg, 0.090 mmol, 1.5 eq), cesium fluoride (18 mg, 0.12 mmol, 2 eq), copper iodide (1 mg, 0.0048 mmol, 0.08 eq) and PdCl₂ (0.4 mg, 0.0023 mmol, 0.04 eq). A solution of P(tBu)₃ (2.0 mg, 0.010 mmol, 0.16 eq) in freshly distilled and degassed DMF (2 mL) was injected via septum. The resulting mixture was stirred at 50 °C for 18 h. After cooling to room temperature, the solution was diluted with dichloromethane and water. The mixture was extracted with dichloromethane (2x). The combined organic layer was washed with brine (2x), dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The crude product was then purified by column chromatography on silica gel (eluent: petroleum spirit/dichloromethane [9/1, v/v] to [3/7, v/v]). 31 mg of the desired compound **IV-18** were obtained as a yellow-orange solid (yield of 53%). ¹H NMR (300 MHz, CDCl₃, 25 °C), δ (ppm): 8.07 (m, 1 H), 7.91 (m, 3 H), 7.80 (d, J= 8.6 Hz, 4 H), 7.73 (d, J= 7.8 Hz, 1 H), 7.69 (d, J= 7.6 Hz, 1 H), 7.64 (dt, J= 1.6 Hz, J= 8.1 Hz, 1 H), 7.40 (d, J= 5.0 Hz, 1 H), 7.16 (dd, J= 3.7 Hz, J= 5.1 Hz, 1 H), 7.10 (d, J= 1.6 Hz, 1 H), 7.03 (m, 5 H), 2.00 (m, 2 H), 1.82 (m, 2 H), 1.51 (s, 18 H), 0.71-1.03 (m, 18 H), 0.67 (t, J= 7.2 Hz, 3 H), 0.44-0.56 (m,

9 H). ¹³C NMR (75 MHz, CDCl₃, 25 °C), δ (ppm): 165.4, 154.1, 153,0 150.8, 145.1, 140.9, 139.6, 133.4, 128.3, 127.9, 127.6, 127.4, 126.6, 126.2, 126.1, 125.9, 125.8, 124.8, 122.4, 122.1, 121.1, 119.5, 80.7, 55.3, 44.8, 44.7, 34.7, 33.4, 28.6, 28.2, 27.3, 26.4, 23.9, 22.9, 22.7, 20.8, 17.5, 14.1, 10.6. HRMS (MALDI-TOF) m/z: [M]⁺ calculated for C₆₁H₇₁N₃O₄S₂: 973.4881; found: 973.4915. Δ = 3.5ppm.

Sensitizer PP1

In a round bottom flask containing **10** (31 mg, 0.032 mmol, 1 eq) under argon was added dichloromethane (6 mL) and then trifluoroacetic acid (2 mL) slowly. The resulting solution was then stirred for 4 h at room temperature. After completion of the reaction monitored by TLC, the crude was concentrated under reduced pressure. The product was obtained as a yellow-orange powder with a yield of 99% (29 mg). ¹H NMR (300 MHz, THF-*d*8, 25 °C), δ (ppm): 8.27 (m, 2 H), 8.11 (m, 2 H), 7.85-8.00 (m, 7 H), 7.60 (d, J= 4.9 Hz, 1 H), 7.36 (m, 1 H), 7.15-7.26 (m, 6 H), 2.18 (m, 2 H), 2.02 (m, 2 H), 1.09 (m, 2 H), 0.85-1.04 (m, 16 H), 0.79 (t, J= 7.1 Hz, 3 H), 0.58-0.66 (m, 9 H). ¹³C NMR (75 MHz, THF-*d*8, 25 °C), δ (ppm): 166.2, 154.0, 153.1, 152.3, 151.0, 150.7, 145.4, 141.0, 139.3, 138.6, 135.5, 132.9, 130.9, 128.3, 127.7, 127.6, 127.4, 126.8, 126.1, 125.5, 125.0, 122.8, 122.1, 121.2, 119.4, 55.3, 44.6, 44.4, 34.7, 34.2, 33.6, 33.5, 29.7, 28.8, 28.1, 27.3, 26.4, 26.4, 22.9, 22.6, 13.6, 10.1, 9.4, 9.4. HRMS (ESI+) m/z: [M+H]⁺ calculated for C₅₃H₅₆N₃O₄S₂: 862.3712; found: 862.3737. Δ =2.9ppm.

Compound 11

In a sealed tube under argon were introduced: compound **3** (150 mg, 0.180 mmol, 1 eq), compound **9** (180 mg, 0.390 mmol, 2.2 eq) in toluene (10 mL). The solution was degassed carefully and Pd(PPh₃)₄ (21 mg, 0.018 mmol, 0.1 eq) was added quickly. The resulting mixture was stirred at 110 °C for 24 h. After cooling to room temperature the solution was concentrated under reduced pressure. The crude product was then purified by column chromatography on silica gel (eluent: petroleum spirit/dichloromethane [6/4, v/v] to [4/6, v/v]). 130 mg of the desired compound **11** were obtained as a red solid (yield of 69%). ¹H NMR (400 MHz, CDCl₃, 25 °C), δ (ppm): 8.13 (m, 2 H), 7.88 (m, 6 H), 7.67 (m, 4 H), 7.44

(m, 2 H), 7.20 (m, 1 H), 7.17 (m, 1 H), 7.10 (m, 5 H), 2.07 (m, 2 H), 1.89 (m, 2 H), 1.60 (s, 18 H), 1.05 (m, 2 H), 0.79-1.01 (m, 16 H), 0.76 (m, 3 H), 0.69 (m, 3 H), 0.58 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃, 25 °C), δ (ppm): 165.4, 152.8, 152.7, 152.6, 151.5, 150.8, 146.4, 145.1, 140.6, 139.4, 138.3, 138.3, 132.4, 130.8, 128.8, 128.0, 127.5, 126.8, 126.0, 126.0, 125.8, 125.2, 125.1, 123.8, 122.3, 121.3, 121.0, 120.0, 80.7, 55.3, 44.7, 34.8, 34.3, 33.7, 33.6, 28.8, 28.2, 27.5, 26.5, 26.5, 23.0, 22.8, 14.2, 14.1, 10.7, 10.1. HRMS (ESI+) m/z: [M]⁺ calculated for C₆₅H₇₃N₃O₄S₃: 1055.4758; found: 1055.4741. Δ = 1.6ppm.

Sensitizer PP2

In a round bottom flask containing **11** (39 mg, 0.037 mmol, 1 eq) under argon was added dichloromethane (5 mL) and then trifluoroacetic acid (1 mL) slowly. The resulting solution was then stirred for 5 h at room temperature. After completion of the reaction monitored by TLC, the crude was concentrated under reduced pressure. The product **PP2** was obtained as a red powder with a yield of 99% (35 mg). ¹H NMR (400 MHz, CDCl₃/MeOD [4/1], 25 °C), δ (ppm): 8.02 (m, 2 H), 7.85 (d, J= 8.3 Hz, 4 H), 7.77 (s, 2 H), 7.59 (m, 4 H), 7.35 (m, 2 H), 6.98-7.13 (m, 7 H), 1.97 (m, 2 H), 1.80 (m, 2 H), 0.68-0.99 (m, 18 H), 0.66 (m, 3 H), 0.56 (m, 3 H), 0.46 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃/MeOD [4/1], 25 °C), δ (ppm): 168.5, 152.9, 152.6, 152.4, 151.4, 151.1, 146.3, 144.7, 140.4, 139.3, 138.5, 138.5, 138.2, 132.4, 131.2, 128.7, 127.9, 127.4, 126.7, 126.3, 126.0, 125.7, 125.1, 124.9, 124.1, 123.7, 122.9, 122.7, 122.1, 121.4, 121.2, 121.0, 119.9, 55.2, 44.6, 34.7, 34.2, 33.6, 33.5, 31.5, 29.6, 28.7, 28.1, 28.1, 27.4, 26.4, 26.3, 22.8, 22.6, 22.5, 13.9, 13.8, 10.5, 9.9, 9.9. HRMS (ESI+) m/z: [M]⁺ calculated for C₅₇H₅₇N₃O₄S₃: 943.3506; found: 943.3494. Δ =1.3 ppm.

Compound 12

In a round bottom flask equiped with an addition funnel and containing compound **11** (50 mg, 0.047 mmol, 1 eq) and mercury caproate (24 mg, 0.057mmol, 1.2 eq) under argon atmosphere was added a mixture chloroform/acetic acid [95/5] (5 mL). The solution was stirred 1 h at room temperature. The solution was then cooled to 0 $^{\circ}$ C with an ice bath and a solution of iodine (14 mg, 0.057 mmol, 1.2 eq) in chloroform (10 mL) was added dropwise over 2 h. After 30 min of additionnal stirring, dichloromethane was added and the solution was washed

with a 10% aqueous solution of sodium hydrogenocarbonate (2x), a saturated aqueous solution of sodium sulfite (2x), and water (2x). The organic layer was then dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure. The compound **12** was obtained as a red solid without further purification (47 mg, yield of 84%). ¹H NMR (400 MHz, CDCl₃, 25 °C), δ (ppm): 8.14 (m, 1 H), 7.86 (m, 5 H), 7.79 (d, J= 7.7 Hz, 1 H), 7.68 (m, 5 H), 7.44 (m, 1 H), 7.34 (d, J= 3.9 Hz, 1 H), 7.15 (m, 1 H), 7.05-7.13 (m, 5 H), 2.05 (m, 2 H), 1.87 (m, 2 H), 1.60 (s, 18 H), 1.03 (m, 2 H), 0.78-0.97 (m, 16 H), 0.75 (m, 3 H), 0.67 (m, 3 H), 0.55 (m, 6 H). ¹³C NMR (100 MHz, CDCl₃, 25 °C), δ (ppm): 165.5, 152.9, 152.5, 151.6, 150.9, 146.8, 145.4, 145.2, 140.7, 138.4, 138.3, 138.2, 137.9, 132.4, 130.9, 129.2, 128.3, 126.5, 126.1, 125.9, 125.5, 125.2, 124.7, 124.0, 122.7, 122.4, 121.5, 121.4, 121.1, 120.1, 80.8, 76.3, 55.4, 44.8, 34.9, 34.4, 33.7, 33.6, 28.9, 28.4, 28.3, 27.6, 26.6, 26.5, 23.1, 22.9, 14.3, 14.2, 10.9, 10.2. HRMS (ESI+) m/z: [M]⁺ calculated for C₆₅H₇₂IN₃O₄S₃: 1181.3724; found: 1181.3716. Δ =0.7 ppm.

Compound 14

In a Schlenk tube were introduced: iodinated compound 12 (40 mg, 0.034 mmol, 1 eq), compound 13 (32 mg, 0.068 mmol, 2 eq), $Pd(PPh_3)_4$ (2 mg, 0.0017 mmol, 0.05 eq) and copper iodide (0.6 mg, 0.0034 mmol, 0.1 eq). The tube was backfilled with argon (5 cycles) and a degassed mixture of toluene /triethylamine [3/1, v/v] (8 mL) was injected via septum. The resulting mixture was stirred at 70 °C for 3 h. After cooling to room temperature, the solution was concentrated under reduced pressure. The crude product was then purified by column chromatography on silica gel (eluent: petroleum spirit/dichloromethane [9/1, v/v] to pure dichloromethane). The wanted compound 14 was obtained as a dark red solid with a yield of 70% (31 mg). ¹H NMR (300 MHz, CDCl₃, 25 °C), δ (ppm): 8.78 (s, 4 H), 8.16 (m, 1 H), 8.01 (d, J= 3.9 Hz, 1 H), 7.87 (m, 6 H), 7.74 (d, J= 8.6 Hz, 2 H), 7.68 (m, 4 H), 7.45 (m, 1 H), 7.40 (d, J= 4.0 Hz, 1 H), 7.35 (d, J= 8.6 Hz, 2 H), 7.15 (d, J= 1.5 Hz, 1 H), 7.09 (m, 5 H), 4.20 (m, 2 H), 2.05 (m, 2 H), 1.88 (m, 2 H), 1.76 (m, 2 H), 1.59 (s, 18 H), 1.24-1.48 (m, 10 H), 0.50-1.10 (m, 33 H). ¹³C NMR (75 MHz, CDCl₃, 25 °C), δ (ppm): 165.4, 162.9, 162.7, 152.8, 152.5, 152.4, 151.5, 150.8, 146.8, 145.1, 141.1, 140.7, 138.1, 134.5, 133.2, 132.5, 131.5, 131.0, 130.8, 129.2, 128.8, 127.2, 127.1, 128.8, 126.5, 126.0, 125.9, 125.1, 124.8, 124.2, 124.0, 123.9, 122.3, 121.0, 120.0, 94.2, 84.3, 80.7, 55.2, 44.7, 41.1, 34.8, 34.3, 33.6, 31.8, 29.3, 29.2, 28.8, 28.3, 28.1, 27.5, 27.1, 26.5, 23.0, 22.8, 22.7, 14.2, 14.1, 14.1, 10.7,

10.0. HRMS (MALDI-TOF) m/z: $[M]^+$ calculated for C₉₅H₉₇N₅O₈S₃: 1531.6494; found: 1531.6539. Δ = 2.9 ppm.

Sensitizer PP2-NDI

In a round bottom flask containing **14** (31 mg, 0.024 mmol, 1 eq) under argon was added dry dichloromethane (3 mL) and then trifluoroacetic acid (3 mL) slowly. Afterwards, the resulting solution was stirred for 5 h at room temperature. After completion of the reaction monitored by TLC, the crude was concentrated under reduced pressure. The resulting product **PP2-NDI** was obtained as a dark red solid with a yield of 96% (27mg). NMR signals were very broad and ill resolved regardless the conditions; however, TLC analysis revealed that the hydrolysis step was quantitative, and the identity of the final molecule was confirmed by HRMS: HRMS (ESI-) m/z: $[M-2H]^{2-}$ calculated for C₈₇H₇₉N₅O₈S₃: 1417.5091; found: 1417.5116. Δ =1.8 ppm.

Photovoltaic devices fabrication

Conductive glass substrates (F-doped SnO₂) were purchased from Solaronix (TEC15, sheet resistance 15 Ω /square). Conductive glass substrates were successively cleaned by sonication in soapy water, then acidified ethanol for 10 min before being fired at 450 °C for 30 min. Once cooled down to room temperature, a solution of nickel acetate (0.5 M) and ethanolamine (0.5 M) in methoxyethanol was spin-coated on FTO substrates, the latter were then fired at 500°C for 30 minutes.⁷⁹ As treated FTO plates were then screen printed with NiO using a home-made paste. The NiO screen-printing paste was produced by preparing a slurry of 3 g of NiO nanopowder (Inframat) suspended in distilled ethanol (10 mL) 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 terpineol (20 mL), followed by slow ethanol removal by rotary evaporation. The dried films were calcined in air at 400 °C for 0.5 h. The electrodes were finally dipped for 30 minutes in a 20 mM nickel acetate and ethanolamine (a few drops to insure solubility) solution at 60°C, rinsed in ethanol and thermally treated at 120°C in air.^{80,81} The prepared NiO electrodes were soaked while still hot (80 °C) in a 0.2 mM solution (CH₂Cl₂/EtOH: 1/1) for each dye during 16 h.

Electrolytes used are composed of: 30 mM I₂, 0.1 M guanidinium thiocyanate, 0.5 M 4*tert*butylpyridine and 0.6 M N-propyl-N'-ethylmethylimidazolium iodide in acetonitrile for

the I_3^-/Γ electrolyte, 0.1 M **Co1**²⁺, 0.1 M **Co1**³⁺ and 0.1 M LiClO₄ in propylene carbonate for cobalt complex as redox shuttle and 0.3 M T₂, 0.9 M T⁻ and 0.1 M LiTFSI for T₂/T⁻ electrolyte. The electrolyte used for tandem dye sensitized solar cells was 0.6 M N-propyl-N'- ethylmethylimidazolium iodide, 0.5 M 4-*tert* butylpyridine, 0.1 M guanidinium thiocyanate and 0.015 M I₂ in acetronitrile. Platinum counter electrodes were prepared by depositing a few drops of an isopropanol solution of hexachloroplatinic acid in distilled isopropanol (2 mg per mL) on FTO plates (TEC7, Solaronix). Substrates were then fired at 375°C for 30 mn. The photocathode and the counter electrode were placed on top of each other and sealed using a thin transparent film of Surlyn polymer (DuPont, 25 µm) as spacer. A drop of electrolyte was introduced through a predrilled hole in the counter electrode by vacuum backfilling, the hole was then sealed by a glass stopper with surlyn. The cell had an active area of 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.

7. References

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Supplementary material for

Synthesis and properties of new benzothiadiazolebased push-pull dyes for p-type dye sensitized solar cells

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Figure S1. J-V curves with different electrolytes I_3^-/Γ^- , **Co1**³⁺/**Co1**²⁺ and T_2/T^-







Electrolyte Co1³⁺/Co1²⁺



Electrolyte T₂/T⁻

Figure S2. J/V curves recorded in the dark for **PP1**, **PP2** and **PP2-NDI** based devices, with T_2/T^- and I_3^-/I^- electrolytes.





Figure S3. Structures of D35 and redox mediators

Figure S4. Overlay of the IPCE for D35-based nDSC and PP2-NDI-based pDSC, with the same electrolyte.



Figure S5. J/V curve of the tandem dye sensitized solar cell with the T_2/T redox mediator



Highlights

- New push pull dyes **PP1** and **PP2** based on a benzothiadiazole-π-trisarylamine skeleton are designed for NiO p-type dye sensitized solar cells (pDSC)
- Highly performant pDSC were obtained owing to a properly vectorialized photoinduced hole transfer, and an intense charge transfer absorption in the visible
- The best performing dye is a dyad **PP2-NDI** bearing a naphthalene-diimide secondary electron acceptor, due to the larger distance between the photo-generated hole in NiO and the electron on the dye, curbing the geminate charge recombination
- The association of a **PP2-NDI** / NiO photocathode and a **D35** / TiO₂ photoanode afforded a tandem DSC with a high photoconversion efficiency of 2.80%

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