Push–Pull N,N-Diphenylhydrazones Bearing Bithiophene or Thienothiophene Spacers as Nonlinear Optical Second Harmonic Generators and as Photosensitizers for Nanocrystalline TiO₂ Dye-Sensitized Solar Cells

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Supporting Information

ABSTRACT: A series of push–pull heterocyclic N,N-diphenylhydrazones were prepared to study the effect of structural modifications (different π-spacers and electron-withdrawing groups) on the optical (linear and nonlinear) and electronic properties of the molecules. The photovoltaic response of dye-sensitized solar cells assembled using nanocrystalline titania photosensitized with the synthesized dyes was also studied. These heterocyclic push–pull conjugated dyes involve N,N-diphenylhydrazones as electron donors linked to bithiophene or thieno[3,2-b]thiophene spacers and were functionalized with carboxylic acid, cyanocetic acid, or dicyanovinyl acceptor groups. A combination of Suzuki–Miyaura cross-coupling, Vilsmeier formylation, and condensation reactions was used to synthesize the intermediates and final products. Density functional theory (DFT) and time-dependent-DFT calculations were used to obtain information on conformation, electronic structure, and electron distribution, both for the free dyes and those adsorbed on TiO₂. The results of this multidisciplinary study indicate that dyes 5b and 6b have the strongest second-order nonlinear optical response with hyperpolarizability values in the range of β = 2330 × 10⁻³⁰ to 2750 × 10⁻³⁰ esu, whereas photovoltaic power conversion efficiencies reach values in the range of 0.7–3.0% for dyes 5a–b and 7c and were enhanced by coadsorbing deoxyxocholic acid (0.8–5.1%).

1. INTRODUCTION

Push–pull heteroaromatic π-conjugated systems are established compounds in materials science, which combine easy synthesis with tunability of structures to produce systems with predictable and unique optoelectronic properties. The molecular arrangement of these D−π−A systems leads to terminal electron donor and acceptor group communication through a π-conjugated bridge. This intramolecular charge transfer (ICT) involves a new low-energy molecular orbital, accessible through visible light excitation, which is responsible for the polarization of the molecule.¹,²

Optoelectronic properties of these push–pull systems may have applications in field-effect transistors,³ light-emitting diodes,⁴ nonlinear optics [second harmonic generation (SHG) and two-photon absorption],⁵–⁷ photovoltaics,⁸–¹³ and near-infrared absorbing dyes.¹⁴

These push–pull systems may be tailored toward specific applications by changing electron donor or acceptor moieties, spacer (conjugation length, planarity, and electronic nature), and the overall chromophore arrangement. An efficient method of tuning the electronic properties of these systems involves incorporation of heterocyclic units, which provide high polarizability, thermal and chemical robustness, and possibilities for further structural changes. In addition, they can behave as both efficient spacers and auxiliary electron donor/acceptor groups. A variety of π-bridges and donor and acceptor groups have been used in the design of heterocyclic push–pull heterocyclic dyes.¹,²

Aromatic hydrazone-based compounds have been studied in several areas of materials chemistry, such as organic nonlinear optical (NLO)¹⁵–¹⁶ and hole-transport materials, and so forth.¹⁹,²⁰ These compounds have been of particular interest because of the easy synthetic access through reaction of carbonyl compounds (particularly aldehydes) with relatively low-cost starting materials, avoiding expensive catalysts. They are also tolerant to the presence of water and/or oxygen. Other
interesting characteristics are the extended conjugation when compared to the corresponding amines, good thermal and chemical stability, and enhancement of charge mobility through delocalization of the terminal nitrogen atom lone pair into the π-conjugated system.\textsuperscript{16–20}

Although application of compounds with a hydrazine moiety as efficient electron donors in bulk-heterojunction solar cells has previously been reported,\textsuperscript{21–25} few have been studied as sensitizing dyes for nanocrystalline TiO\textsubscript{2} dye-sensitized solar cells (DSSCs).\textsuperscript{26–28} The excellent electronic properties of the thiophene moiety have led to its widespread application in the design of ICT chromophores.\textsuperscript{29,30}

On the basis of the interesting results reported by us and other groups,\textsuperscript{1,2,15–18,24–28} we have synthesized five organic dyes bearing electron-rich heteroaromatic groups (N,N-diphenylhydrazidine and thiophene) as the donor moiety or/π-spacer and carboxylic, cyanoacetic acid, or dicyanovinyl moieties as the strong electron-withdrawing/-anchoring groups. Their optical and redox properties have been evaluated, and they have been tested in DSSC photovoltaic devices.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization. A series of push–pull heterocyclic chromophores were prepared to study the effect of different spacers (bithiophene and thiophene) and electron-withdrawing moieties (carboxylic acid, cyanoacetic acid, and dicyanovinyl) on their linear and NLO properties, redox behavior, and potential as sensitizers in DSSCs based on nanocrystalline titania. All of the compounds bear a N,N-diphenylhydrazidine donor unit that was chosen because of its high charge mobility properties as an electron donor.\textsuperscript{29} The thiophene units in the π-spacer show excellent charge-transfer properties, efficient π-conjugation, and low geometrical relaxation upon oxidation.\textsuperscript{30–34}

The aldehyde precursor \textsuperscript{2}c was prepared in good yield (53%) by Suzuki–Miyaura cross-coupling of 5-bromothiophene-2-carboxylic acid and 5-formyl-2-thiopheneboronic acid. Intermediates \textsuperscript{3}a–b and push–pull chromophore \textsuperscript{7}c were synthesized in moderate to good yields (55–72%) through condensation of the respective aldehydes \textsuperscript{2}a–c with N,N-diphenylhydrazidine \textsuperscript{1} in ethanol. The intermediate aldehydes \textsuperscript{4}a–b were obtained (45–58% yields) by Vilsmeier–Haack formylation. Knoevenagel condensation (piperidine catalyst) in refluxing ethanol of the aldehydes \textsuperscript{4}a–b with 2-cyanoacetic acid gave the push–pull chromophores \textsuperscript{5}a–b in fair to good yields (27–58%), whereas dyes \textsuperscript{6}a–b were prepared in fair yields (22–29%) by condensation of the same aldehydes with malononitrile (Scheme 1).

Recently, the synthesis of precursor \textsuperscript{3}a was reported by Roncali and collaborators through condensing N,N-diphenylhydrazine with aldehyde \textsuperscript{2}a, in 63% yield, using different experimental conditions: MeOH/tetrahydrofuran in the presence of sodium acetate. Aldehyde \textsuperscript{4}b was also reported, in 37% yield, using a one-step methodology by condensing N,N-diphenylhydrazine with 5,5′-diformylbibithiophene. The same investigators also published the synthesis of dyes \textsuperscript{6}a–b using different reaction conditions (NET\textsubscript{3} as the base and CHCl\textsubscript{3} as the solvent).\textsuperscript{33}

The structures of these compounds were confirmed by standard procedures (detailed characterization and Table S1 with experimental data in the Supporting Information).

2.2. Electrochemical Study. To obtain energies of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) redox properties of the compounds, \textsuperscript{5}a–b and \textsuperscript{7}c were studied using cyclic voltammetry (CV). In DSSCs, dye N719 is most commonly used; its band gap energy is appropriate for absorption in the visible region of the solar spectra; energies of LUMO and HOMO fit well for electron injection into TiO\textsubscript{2} and regeneration of the dye. Data on the electrochemical behavior of N719 are presented as a “reference”. The energies of HOMO and LUMO of \textsuperscript{5}a–b and \textsuperscript{7}c were calculated. The energy level of ferrocene (4.39 eV) was used as the reference. Table 1 summarizes the data. For compounds \textsuperscript{5} and \textsuperscript{7}, the redox behavior is reversible; whatever scan rate of potential is applied, the potentials of cathodic and anodic peaks of current remain constant. Potentials for oxidation of compounds \textsuperscript{5}a, \textsuperscript{5}b, and \textsuperscript{7}c are 0.73, 0.67, and 0.64 V, respectively. These potentials are higher than the potential of the 3Γ/1Γ′ couple (0.42 V), which in the case of application in solar cells, reduces back transfer of electrons to the electrolyte.\textsuperscript{48,49} The oxidation potential clearly depends on the electronic nature of the heteroaromatic spacer unit: the stronger the auxiliary electron-donating ability, the easier it is to oxidize the molecule. The bithiophene derivative \textsuperscript{5}b displays the lowest oxidation potential (highest energy of HOMO), suggesting a slightly stronger electron-donating ability when compared to compound \textsuperscript{5}a (this is in accordance with the UV–vis spectral data). The LUMO level of the dyes indicates the thermodynamic possibility of the electron injection into the conduction band of TiO\textsubscript{2} such that the LUMO level of the
Table 1. Electrochemical Data for the Dyes 5a–b, 7c, and N719

<table>
<thead>
<tr>
<th>Cpd</th>
<th>reduction /V</th>
<th>oxidation /V</th>
<th>$E_{\text{HOMO}}$ /eV</th>
<th>$E_{\text{LUMO}}$ /eV</th>
<th>band gap /eV</th>
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</thead>
<tbody>
<tr>
<td>5a</td>
<td>−1.94</td>
<td>0.73</td>
<td>−5.12</td>
<td>−2.45</td>
<td>2.67</td>
</tr>
<tr>
<td>5b</td>
<td>−1.74</td>
<td>0.67</td>
<td>−5.06</td>
<td>−2.65</td>
<td>2.41</td>
</tr>
<tr>
<td>7c</td>
<td>−2.29</td>
<td>0.64</td>
<td>−5.02</td>
<td>−2.20</td>
<td>2.92</td>
</tr>
<tr>
<td>N719</td>
<td>−2.04</td>
<td>0.46</td>
<td>−4.85</td>
<td>−2.35</td>
<td>2.50</td>
</tr>
</tbody>
</table>

$^a$Measured in 1.0 mM solution of the dye in DMF with the addition of 0.1 M tetraethylammonium tetrafluoroborate. Glassy carbon was used as a working electrode. Scan rate of potential: 0.01 V s$^{-1}$. Potentials (E) are indicated with respect to Fc$^+/Fc$. $E_{\text{pa}}$ and $E_{\text{pc}}$ stand for the potentials of anodic and cathodic peaks, respectively. $E_{\text{LUMO}} = -(E_{\text{ox}}+4.39)$ (eV) and $E_{\text{HOMO}} = -(4.39 + E_{\text{red}})$ (eV). $^b$Calculated as the difference between the onset potentials of oxidation and reduction.

Table 2. UV–Visible Absorption and Fluorescence Data for N,N-Diphenylhydrazone Derivatives 3–7 in Ethanol Solution at Room Temperature

<table>
<thead>
<tr>
<th>Cpd</th>
<th>$\lambda_{\text{max/nm}}$</th>
<th>$\epsilon$/M$^{-1}$ cm$^{-1}$</th>
<th>$\Phi_f$</th>
<th>Stokes shift/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>368</td>
<td>24 867</td>
<td>428</td>
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</tr>
<tr>
<td>3b</td>
<td>373</td>
<td>26 060</td>
<td>454</td>
<td>0.20</td>
</tr>
<tr>
<td>4a</td>
<td>410</td>
<td>29 750</td>
<td>480</td>
<td>0.01</td>
</tr>
<tr>
<td>4b</td>
<td>440</td>
<td>23 588</td>
<td>536</td>
<td>0.01</td>
</tr>
<tr>
<td>5a</td>
<td>435</td>
<td>30 740</td>
<td>537</td>
<td>0.01</td>
</tr>
<tr>
<td>5b</td>
<td>456</td>
<td>20 141</td>
<td>574</td>
<td>0.03</td>
</tr>
<tr>
<td>6a</td>
<td>423</td>
<td>26 766</td>
<td>564</td>
<td>0.01</td>
</tr>
<tr>
<td>6b</td>
<td>448</td>
<td>19 221</td>
<td>591</td>
<td>0.01</td>
</tr>
<tr>
<td>7c</td>
<td>416</td>
<td>12 562</td>
<td>501</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Figure 1. Normalized absorption (full solid lines) and emission (dashed lines) spectra for compounds 4–7 in ethanol at room temperature.
compounds as well as some compounds containing carbonyl groups and nitrogen heterocycles. As expected, a red shift of the emission of the compounds is observed upon increasing the strength of the acceptor group (aldehyde < carboxylic acid < cyanoacetic acid < dicyanovinyl). Thieno[3,2-b]thiophene 4a, 5a, and 6a show emissions at 480, 519, and 564 nm, respectively, whereas bithiophenes 4b, 5b, 6b, and 7c exhibit emissions at 536, 574, 591, and 501 nm, respectively. A bathochromic shift is also observed upon increasing the π-conjugation path length through the bithiophene spacer, comparing compound 4a with 4b (7 nm), compound 5a with 5b (52 nm), and compound 6a with 6b (18 nm). All of the studied push-pull systems show large Stokes’s shifts (3557–5910 cm⁻¹), indicating that significant structure relaxation occurs in the excited state upon absorption. Moreover, the compounds functionalized with stronger electron-withdrawing cyanoacetic acid and dicyanovinyl moieties 5–6 exhibit larger Stokes’s shifts than the corresponding aldehyde precursors 4. This is consistent with the possibility of increased ICT upon absorption, particularly in the case of the dicyanovinyl moieties for which the Stokes shift increase is greater than 50%.

2.3.2. NLO Properties. Hyper-Rayleigh scattering (HRS) was used to characterize the molecular first hyperpolarizabilities β of push-pull N,N-diphenyldihydrazone derivatives 5–7. The incident laser beam had a fundamental wavelength of 1064 nm, and the chromophores were dissolved in dioxane. The mean hyperpolarizability values, β, were determined by comparison with a p-nitroaniline (pNA) reference solution. The extent that the second harmonic signal might be contaminated by multiphoton-induced fluorescence was taken into account by measuring the HRS signal over different spectral bandwidths (see Supporting Information for more details). The static hyperpolarizabilities β₀ were estimated via a simple two-level model neglecting damping. Both an increase in the π-conjugation of the spacer and an intensification of the electronic acceptor ability of the withdrawing group clearly influence the nonlinearities of compounds 4–7 as quantified in Table 3. First, the measured β values show that the bithiophene spacer leads to higher molecular hyperpolarizability values than the thieno[3,2-b]thiophene moiety. Therefore, aldehyde 4b has a higher β value (β = 290 × 10⁻³⁰ esu) than 4a (β = 205 × 10⁻³⁰ esu), as does cyanoacetic acid 5b (β = 2330 × 10⁻³⁰ esu) when compared to 5a (β = 930 × 10⁻³⁰ esu) and dicyanovinyl derivative 6b (β = 2750 × 10⁻³⁰ esu) in comparison with 6a (β = 265 × 10⁻³⁰ esu). The static hyperpolarizability β₀ values of the compounds follow the same trend. The more extensive π-conjugation and stronger auxiliary electron-donating ability of the bithiophene moiety are probably the main reasons for these trends. We also notice a general increase of the hyperpolarizability β as the electron-accepting ability is increased and as the electronic conjugation of the acceptor end moiety becomes larger. In the case of compounds bearing thieno[3,2-b]thiophene (4a, 5a, and 6a), the SHG response is enhanced by an increase of the acceptor group strength upon changing the aldehyde group (β = 205 × 10⁻³⁰ esu for 4a) to a dicyanovinyl group (β = 265 × 10⁻³⁰ esu for 6a) and then for a cyanoacetic acid moiety (β = 930 × 10⁻³⁰ esu for 5a). A similar tendency is observed in compounds bearing bithiophene as the spacer (4b, 5b, 6b, and 7c). Derivative 4b shows the lowest hyperpolarizability β, followed by the carboxylic acid 7c.

Table 3. UV–Vis Absorption Data in 1,4-Dioxane and β and β₀ Values for Chromophores 4–6 and 7c

<table>
<thead>
<tr>
<th>Cpd</th>
<th>λ max/nm</th>
<th>ε/M⁻¹ cm⁻¹</th>
<th>β/M³ cm⁻² esu</th>
<th>β₀/M³ cm⁻² esu</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>408</td>
<td>30 871</td>
<td>205</td>
<td>72</td>
</tr>
<tr>
<td>4b</td>
<td>438</td>
<td>28 010</td>
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<td>77</td>
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<tr>
<td>5a</td>
<td>464</td>
<td>31 534</td>
<td>930</td>
<td>180</td>
</tr>
<tr>
<td>5b</td>
<td>486</td>
<td>20 125</td>
<td>2330</td>
<td>300</td>
</tr>
<tr>
<td>6a</td>
<td>423</td>
<td>27 032</td>
<td>265</td>
<td>81</td>
</tr>
<tr>
<td>6b</td>
<td>447</td>
<td>20 022</td>
<td>2750</td>
<td>910</td>
</tr>
<tr>
<td>7c</td>
<td>422</td>
<td>12 444</td>
<td>370</td>
<td>114</td>
</tr>
<tr>
<td>pNA</td>
<td>352</td>
<td>40.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Wavelength of the absorption maximum of the respective compound when dissolved in dioxane. Average hyperpolarizability values, β, reported in the T-convention. Estimate of the static hyperpolarizability using the two-level model, β₀ = β(1 − (λ max/1064 nm)²)(1 − (λ max/532 nm)²), and neglecting damping factors.

Table 3. UV–Vis Absorption Data in 1,4-Dioxane and β and β₀ Values for Chromophores 4–6 and 7c

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<td>4a</td>
<td>408</td>
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<td>205</td>
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<tr>
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<td>12 444</td>
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<tr>
<td>pNA</td>
<td>352</td>
<td>40.1</td>
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</tbody>
</table>

*Wavelength of the absorption maximum of the respective compound when dissolved in dioxane. Average hyperpolarizability values, β, reported in the T-convention. Estimate of the static hyperpolarizability using the two-level model, β₀ = β(1 − (λ max/1064 nm)²)(1 − (λ max/532 nm)²), and neglecting damping factors.
could be due to the longer (dashed lines) and with the DCA coadsorbent molecule.

only the higher energy photons from the spectral region 350–450 nm are able to turn the dye to its photoexcited state and contribute to photocurrent. However, this could turn to the advantage of this dye for “greenhouse” concept, where high transparency of the integrated photovoltaic device is eventually important.

DSSCs prepared using dyes 5a–b show very similar photovoltaic efficiencies: 2.98% for 5a and 3.01% for 5b. The slightly higher efficiency of the DSSC sensitized with 5b dye (about 33% of the efficiency of the DSSC with N719 dye), bearing a bithiophene moiety as the π-spacer/auxiliary electron donor, results from the enhanced $j_{SC}$ (6.77 mA cm$^{-2}$) that could be due to the longer π-conjugation of the sensitizing dye and lower electronic band gap when compared to dye 5a.

To enhance the efficiency of the DSSCs sensitized with dyes 5a–b and 7c, we used coadsorption with DCA. Bile acids such as DCA and chenodeoxycholic acid are able to improve the efficiency of the cells because of the reduction of dye aggregation on the surface of TiO$_2$, suppressing dark current and improving electron lifetime.

The photovoltaic response of the cells with dyes 5a and 7c was increased slightly by the addition of DCA as the coadsorbent (from 2.98 to 3.22% for dye 5a and from 0.72 to 0.79% for dye 7c), whereas the efficiency of the cell with dye 5b improved significantly—from 3.01 to 5.10%. It can be seen from Table 4 and Figure 2 that the addition of DCA does not affect $V_{oc}$ of the cells based on dyes 5a and 7c—the variations are within the statistical deviation. The slight enhancement of the performance of these cells is due to the improvement of the FF via suppressing the dark current. At the same time, for dye 5b, coadsorption of DCA leads to noticeable increase of $V_{oc}$.

It is noteworthy that the addition of DCA to the sensitization solutions causes perceptible bathochromic shifts in the transmittance and absorption spectra for dyes 5a–b (Figure 4).

This bathochromic shift is accompanied by a slight increase of the quantum yield above 550 nm for the cell based on dye 5a. Noteworthy, a pronounced improvement of quantum yield above 550 nm for the cell based on dye 5b was observed (Figure 4). The overall performance of the DSSC with dye 5b coadsorbed with DCA was found to be 5.01%, which is promising for metal-free organic dyes.

### 2.5. Computational Studies.

The metal-free organic sensitizers 5a–b and 7c considered in our study have many possible conformations. Different conformers can have very different degrees of conjugation; therefore, it is important to determine the lowest energy conformers responsible for the observed absorption spectra of the dyes. For dyes 5a and 5b, 12 conformers were considered in each case, differing in the relative arrangements of the carboxylic acid, cyano, bithiophene (or thienothiophene), and N,N-diphenylhydrazine groups. For dye 7c, we investigated the structures and energies of four different conformers. For dyes 5b and 7c, a simplification was introduced by considering only the thiophene–thiophene trans conformers. This is justified in view of previous studies, which showed that the cis conformation usually accounts for ca. 10% of the population of conformers in this type of structures. Figure S2 (Supporting Information) shows the most stable conformers of these dyes and their relative energies calculated at the density functional theory (DFT) level. The energy differences found for these forms indicate a population of about 58% for conformer 5a-I, 77% for conformer 5b-I, and 53% for conformer 7c-I. Because these are the dominant conformers, our subsequent analysis will be carried out for these forms, and for simplicity, we will

![Figure 3](image3.png)

**Figure 3.** Spectra of IPCE for the cells assembled using N719, 5a–b, and 7c dyes. The sensitization was in 0.5 mM ethanol solutions of the corresponding dye (dashed lines) and with 50 mM DCA as an additive for coadsorption (solid lines).

![Figure 2](image2.png)

**Figure 2.** Current–voltage characteristics recorded under illumination and in the dark for the DSSCs assembled using synthesized dyes 5a–b and 7c (dashed lines) and with the DCA coadsorbent molecule.
refer to conformers 5a-I, 5b-I, and 7c-I as dyes 5a, 5b, and 7c, respectively.

Figure 5 presents the structures of the dominant conformers. In the three dyes, the cyano and the carboxylic groups are coplanar with the thienothiophene (in 5a) or bithiophene (in 5b and 7c) \( \pi \)-bridges, showing strong conjugation between the \( \pi \)-orbitals of these groups. This is convenient because it will improve the efficiency of electron transfer from the bridge to the electron acceptor. Dye 7c is slightly distorted in the region between the donor and the \( \pi \)-bridge.

Figure 6 shows the DFT-calculated energies for the frontier molecular orbitals of the three dyes. The larger extension of the conjugation in the chain in 5b leads to a smaller band gap for this dye. Dye 7c has its maximum absorption blue-shifted relative to 5a and 5b. The calculated maximum appears at 399 nm (in ethanol solvent, the experimental value is 416 nm), and as with dyes 5a and 5b, the main contribution is a HOMO \( \rightarrow \) LUMO excitation (86%). From Figure 7, one can see the type of the orbitals involved in these transitions. The HOMOs are

The UV–vis absorption spectra (vertical electronic excitations) were calculated for the free dyes at the time-dependent-DFT (TD-DFT)/CAM-B3LYP level, and the main contributions to the transitions with maximum absorption involve the HOMO \( \rightarrow \) LUMO (85%) with small contributions from HOMO \( \rightarrow \) LUMO (8%) and HOMO \( \rightarrow \) LUMO + 1 (3%) excitations. Dye 7c has its maximum absorption blue-shifted relative to 5a and 5b. The calculated maximum appears at 399 nm (in ethanol solvent, the experimental value is 416 nm), and as with dyes 5a and 5b, the main contribution is a HOMO \( \rightarrow \) LUMO excitation (86%). From Figure 7, one can see the type of the orbitals involved in these transitions. The HOMOs are
π orbitals, mainly localized on the donor and the thienothiophene (in 5a) or bithiophene (in 5b and 7c) π-bridges, whereas the LUMOs are π* orbitals essentially on the acceptor group and on the π-bridges. The HOMO − 1 → LUMO and HOMO → LUMO + 1 excitations tend to decrease the charge separation between the ground and excited states in these dyes; however, their contributions to the transition are very small. Therefore, there is efficient charge transfer between the donor and the acceptor upon excitation.

Adsorption of the dye on TiO₂ causes a reorganization of the electronic states of the semiconductor.⁶¹−⁶³ This can affect the electronic absorption spectra of the dyes and also the efficiency of injection of electrons into TiO₂. It is, therefore, important to evaluate the effect of adsorption of the dyes on their structural and electronic properties at the interface. Because of computational limitations, we only carried out this analysis for the dye 5a adsorbed on TiO₂. Two types of approaches have been used to model the dye−TiO₂ interface. One is based on the simulation of the dye adsorbed to an infinitely large particle of TiO₂, in one or multiple dimensions, employing a periodic condition and using plane-wave basis sets.⁶¹ The second approach considers the dye adsorbed to an isolated cluster of (TiO₂)ₙ, and the calculations use a localized basis set.⁶³ Both methods present advantages, and in our study, we have used the second one. The size of the cluster, (TiO₂)ₙ₀, and the bidentate mode of adsorption in which the dye is covalently linked to a Ti atom of the cluster through the two oxygen atoms of the anchoring carboxylic group were also chosen based on the literature.⁶²,⁶₄,⁶₉,⁷₀ To keep electroneutrality of the system, the hydrogen atom coming from deprotonation ⁺ of the anchoring carboxylic group was linked to a cluster oxygen atom.⁶³,⁶⁶ The geometry of the 5a/TiO₂ system was optimized at the DFT level; the effect of dye adsorption on the energy levels of the orbitals is presented in Figure 8. The LUMO and the next virtual orbitals in the combined 5a/TiO₂ system are stabilized relative to the same orbitals of the free dye. This is a consequence of the introduction of additional electronic states by the semiconductor. The HOMO and the next occupied orbitals are also slightly stabilized. Interestingly, however, there is no shift in the absorption maximum of the dye in the combined system, as we can see from Table 5. For the dye 5a adsorbed to (TiO₂)ₙ₀, TD-DFT calculations estimate an absorption maximum at 446 nm, the same value as for the free dye. The maximum absorption transition in the combined 5a/TiO₂ system has now significantly different contributions. Two dominant contributions come from the HOMO → LUMO (37%) and HOMO → LUMO + 1 (36%) excitations, together with minor contributions from HOMO → LUMO + 1 (4%), HOMO − 1 → LUMO (4%), HOMO → LUMO + 4 (4%), HOMO → LUMO + 6 (4%), and HOMO − 1 → LUMO + 3 (3%).

It should be noted that these energy gaps are different in the two systems. Smaller contributions come also from excitations with larger energy gaps, such as HOMO → LUMO + 25, HOMO → LUMO + 26, HOMO → LUMO + 27, and so forth, which are absent in the case of the free dye. The sum of all of these contributions in the case of 5a/TiO₂ gives a resulting vertical excitation energy which is similar to one of the free dye.

Although their energy suffers slight changes, the HOMO and HOMO − 1 in the combined 5a/TiO₂ system (Figure 9) are essentially equivalent to these orbitals in the free dye. In contrast, the LUMO and the remaining virtual orbitals involved in the maximum absorption transition are localized predominantly on the cluster. The LUMO + 3, LUMO + 4, and LUMO + 6 also extend to the acceptor and π-bridge. The distribution of electron density in these orbitals shows that there will be efficient electron injection from the excited dye into TiO₂ in a DSSC.

To discuss further the relation between the performance of the chromophores as sensitizers for TiO₂ DSSCs and their second-order NLO response, we focus on a comparison between compounds 5a and 5b. These chromophores differ only in their π-electron bridge and should have similar coupling efficiencies for electron transfer to the TiO₂ substrate. Given the tendency of many D−π−A molecules to form π-stacked aggregates on the surface of TiO₂ clusters, which will encourage the back transfer of electrons and, consequently, decrease DSSC efficiency, we further restrict our attention to the measurements using the coabsorber DCA, known for its ability to dissociate π-aggregates. The ratio of the efficiency of the 5b + DCA DSSC to that of the 5a−DCA DSSC is 5.10%:3.22% ≈ 1.6, roughly equal to the ratio of the extrapolated hyperpolarizabilities, 300:180 ≈ 1.7. Interestingly, the DFT-estimated oscillator strengths of the first singlet transition listed in Table 5 indicate that chromophore 5a has a stronger dipole optical transition moment than chromophore 5b. This suggests that the asymmetry in the optical field-induced polarizability of chromophore 5b is greater, which

Figure 7. B3LYP/6-31G(d,p) frontier molecular orbitals of the free dyes 5a, 5b, and 7c.
might facilitate the transfer of photoexcited electrons from the donor to the substrate. We note that the DFT study carried out on chromophore 5a coupled to a TiO2 cluster indicated that because of the interaction between the chromophore and the substrate, the character of the first singlet transition changed; a substantial mixing of the LUMO + 3 state was accompanied by a strong reduction in the participation of the LUMO state (see Table 5). As the electron density of LUMO + 3 extends far into the π-bridge, this could result in less efficient electron collection by the substrate. The existence of a stronger charge-transfer asymmetry in chromophore 5b might counteract this delocalization of the electron density from the TiO2 cluster, promoting higher DSSC efficiencies.

3. CONCLUSIONS

N,N-Diphenylhydrazone derivatives 3–7 were obtained in fair to good yields, using commercially available precursors and
simple, convenient synthetic and purification procedures. Condensation of aldehydes 2a–c with N,N-diphenylhydrazine gave intermediates 3a–b and 7c. Further functionalization of precursors 3a–b through Vilsmeier formylation allowed the preparation of formyl derivatives 4a–b that, through Knovenagel condensation, gave the push–pull compounds 5–6.

Experimental and theoretical characterization of the absorption, fluorescence, and NLO and electrochemical properties of the systems were carried out as a means to evaluate their potential as photosensitizers for nanocrystalline TiO2-based DSSCs. The effect of different π-spacers and acceptor groups was evaluated. These comparative studies demonstrate that the incorporation of the bithiophene π-bridge enhances the electron donor effect when compared with thienothiophene and that the dicyanovinyl acceptor group, although less conjugated than cyanoacetic acid and a weaker electron-withdrawing moiety, induces less distortion to the heterocyclic system, which can be advantageous.

Chromophores 5b and 6b exhibit the highest hyperpolarizability β (2330 × 10−30 esu for 5b, 2750 × 10−30 esu for 6b). The lower hyperpolarizability β value of 5b, which is the more strongly conjugated system, could be attributed to the distorted conformation of the π-system due not only to the bithiophene spacer but also to the cyanoacetic acid moiety.

Compound 5b, bearing a bithiophene π-spacer, exhibits the best conversion efficiency (3.01%) when used as a sensitizer for nanocrystalline titania in DSSCs because of the lower electronic band gap and longer electronic band gap and longer π-conjugation of the sensitizing dye. Studies of coadsorption were performed by adding DCA to the sensitizing mixtures, revealing slight improvements for nanocrystalline titania in DSSCs because of the lower p-conjugation of the sensitizing dye and longer electronic band gap and longer π-conjugation of the sensitizing dye. Studies of coadsorption were performed by adding DCA to the sensitizing mixtures, revealing slight improvements for nanocrystalline titania in DSSCs because of the lower electronic band gap and longer π-conjugation of the sensitizing dye.

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. N,N-Diphenylhydrazine hydrochloride, 5-bromothiophene-2-carboxylic acid, thiophene-3,2-b]thiophene-2-carbaldehyde, 2,2′-bithiophene-5-carboxaldehyde, phosphorous oxychloride, malononitrile, and 2-cyanoacetic acid were obtained from Aldrich, whereas 5-formylthiopheneboronic acid was obtained from Acros Organics. All commercial reagents and solvents were used without further purification. The progress of the reaction was checked by means of thin-layer chromatography on 0.25 mm thick precoated silica plates (Merck Fertigplatten Kieselgel 60 F254); the spots were visualized using UV light. Silica gel column chromatography (Merck Kieselgel, 230–400 mesh) was used in the purification of the compounds. NMR spectra were performed on a Bruker Avance II 400 (working frequency of 400 MHz for 1H and 100.6 MHz for 13C), and the solvent peak was used as the internal reference. The solvents are specified in parenthesis before the chemical shifts values (δ relative to tetramethylsilane). Peak assignments were obtained by comparison of chemical shifts, peak multiplicities, and J values and were sustained by spin decoupling-double resonance and bidimensional heteronuclear multiple bond correlation and heteronuclear multiple quantum coherence techniques. Infrared spectra were obtained on a BOMEM MB 104 spectrophotometer. UV–vis absorption spectra were recorded with a Shimadzu UV/2501PC spectrophotometer. Fluorescence spectra were obtained with a FluoroMax-4 spectrofluorometer, and relative fluorescence quantum yields were determined using the reference standard fluorescein in 0.1 M aqueous solution of NaOH (Φe = 0.79)72 or 9,10-dicyanovinylanthracene in ethanol.73 Melting points were determined on a Gallenkamp machine. Mass spectra analysis was performed at the C.A.C.T.I.—Unidad de Espectrometría de Masas of the University of Vigo, Spain. The experimental procedures for the synthesis of precursor 2, N,N-diphenylhydrazine derivatives 3a–b, 7c, aldehydes 4a–b, the final push–pull cyanoacetic acid 5a–b, and dicyanovinyl derivatives 6a–b are described in the Supporting Information.

4.2. Cyclic Voltammetry. Autolab PGSTAT302N was used for electrochemical measurements. The measurements were performed in a three-electrode cell. Glassy carbon served as the working electrode, Pt was as the counter-electrode, and the reference was Ag/AgCl. Solutions were prepared using dry dimethylformamide (DMF). Concentrations of the dyes were 1 mM. [NBu4][BF4] (0.1 M) was added to achieve sufficient conductivity. All solutions were deaerated by bubbling of N2. As an internal redox reference, Fc+/Fc was used.42,74

4.3. NLO Measurements. The orientationally averaged first hyperpolarizability β of the push–pull chromophores 4–7 was characterized by measuring the intensity of HRS provoked by incident q-switched laser pulses with a pulse duration of approximately 12 ns and an energy of 2 mJ. The experimental setup has been previously described31,38 and is based on the pioneering work of Clays and Persoons,50 (see Supporting Information for further details).

4.4. Preparation and Characterization of DSSCs. DSSCs were prepared as described in the Supporting Information. The photovoltaic performance was obtained with an Oriel Class solar simulator and a ZENNIUM workstation, using a metal mask with an aperture area of 0.25 cm², as previously reported.12 (See Supporting Information for further details).

4.5. Computational Studies. DFT calculations were used to obtain the geometries and optoelectronic properties of the dyes 5a, 5b, and 7c. The geometries of the free dyes were optimized with the B3LYP exchange correlation functional (combination of the hybrid exchange functional of Becke75 together with the correlation functional LYP76), using the all-electron 6-31G(d,p) double-ζ plus polarization basis sets for all atoms. No symmetry constraints were imposed and the polarizable continuum model77,78 was used to account for the effects of chloroform as the bulk solvent. The molecular structures of the most stable conformers of the dyes were also optimized with the CAM-B3LYP79 functional. The harmonic vibrational frequencies were calculated to assess the nature of the optimized stationary points found in the potential energy surface and all were confirmed to be true minima (i.e., with no imaginary frequencies). The properties of the dye 5a adsorbed to a (TiO2)9 cluster were also calculated. The initial geometry for the (TiO2)9 cluster was obtained from previous theoretical studies.80,81 This structure was then optimized using the B3LYP functional and the Los Alamos effective core potential plus double-ζ basis set (LANL2DZ)82–84 on titanium and the 6-31G(d,p) basis set for oxygen. The same computational procedure was used to optimize the geometry of the dye/TiO2...
combined system. TD-DFT calculations were carried out to analyze the absorption spectral properties of the free dyes and of the dye/TiO₂ system and also to calculate the vertical excitation energies for the lowest singlet excited states of the systems. The CAM-B3LYP⁷⁹ functional and the 6-311G(d,p) triple-ζ plus polarization basis sets were used in these calculations. The bulk solvent effects of chloroform were also considered in the TD-DFT calculations. All calculations were carried out using the GAMESS-US code.⁸⁵

■ ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01045.

Synthesis and characterization of compounds 3–6 and 7c; experimental procedures concerning the synthesis; NLO measurements; preparation and evaluation of the performance of DSSCs and figures of optimized geometries and relative energies of the minima for dyes 5a, 5b, and 7c [DFT B3LYP/6-31G(d,p)]; and photocurrent–voltage of the cells assembled using dyes 5a–b and 7c (PDF)

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