Benzo[1,2-b:4,5-b’]difuran-based sensitizers for dye-sensitized solar cells†

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Two BDF-based organic sensitizers, as first examples for their use in dye-sensitized solar cells, are prepared and characterized. They yield promising power conversion efficiencies of up to 5.5% and high open circuit voltages up to 0.82 V. This work demonstrates that the BDF chromophore acts as an effective donor in organic sensitizers.

Dye-sensitized solar cells (DSSCs) as low cost alternatives to traditional photovoltaics have attracted the interest of scientists from different disciplines, and their overall performances developed very rapidly day by day.1–4 Despite the great achievement of Ru(ii)-based dyes showing a power conversion efficiency (PCE) of up to 12%,5 much effort has been devoted to the attainment of metal-free organic dyes due to their low cost, ease of synthesis, structural diversity, and remarkably high optical extinction coefficients. Consequently, a large number of organic dyes, typically with a donor–π-acceptor (D–π–A) configuration, have extensively been investigated for DSSCs.1–7 In practice, a judicious variation of the molecular architectures of the donor fragments as well as of the π-linkers between the donor and acceptor fragments of the dyes, has been the most popular strategy to tailor the frontier orbital energy levels, which finally leads to the formation of dyes with broad and intense optical absorption patterns.8,9 Various molecular scaffolds such as triarylamine, carbazole, porphyrin, and indoline, have been used as attractive components in organic sensitizers. To the best of our knowledge, within this context there has been no report on systems featuring a benzo[1,2-b:4,5-b’]difuran (BDF) chromophore.

BDFs have proven to be excellent components in organic field-effect transistors (OFETs) and organic light-emitting diodes (OLEDs) by virtue of their π-type semiconductor characteristics, intrinsic optical properties and high hole mobility.10,11 It is noteworthy that their cationic radicals formed by a one-electron oxidation, show an intriguing stability.12,13 Thus, the BDF-based dyes are expected to have an enhanced stability in photo-induced electron transfer processes from the dyes to TiO2. For an efficient design of conjugated D–π–A dyes, one of the key issues relates to the synthesis of properly functionalized BDFs, which has rarely been exploited due to the associated synthetic challenges. In previous studies we have developed efficient synthetic routes to fully functionalized BDF derivatives.12–16 On this basis, we have been able to obtain two π-conjugated dyes (Fig. 1) that feature the BDF donor linked to one (Dye-1) and two (Dye-2) standard cyanocrylic acid acceptors. To date, studies on the effect of the number and the positioning of a cyanocrylic acid anchoring group on the cell performance are quite scarce.17,18 We report herein the synthesis and DSCS performance of Dye-1 and Dye-2. This work elaborates on the impact of the number of cyanocrylic acid anchoring groups on the overall efficiencies of solar cells based on BDF donors.

As illustrated in Scheme 1, two new dyes were synthesized in good yields as red solids via a Knoevenagel reaction with cyanacrylic acid. The corresponding aldehyde precursor II was readily obtained from I14 in 74% yield by reaction with one equivalent of 4-bromobenzaldehyde under standard Sonogashira conditions. Similarly, a Sonogashira reaction of III12,13 with 4-ethynylbenzaldehyde was accomplished to afford the dialdehyde IV.19 The target dyes and intermediate compounds have been fully characterized. Their NMR spectroscopic and
mass spectrometric data are consistent with their proposed structures. Both dyes are polycrystalline as confirmed by the powder X-ray diffraction patterns (see ESI†).

The optical and redox properties of the new dyes are listed in Table 1. Their electrochemical properties in CHCl₃ were investigated by cyclic voltammetry (CV). Dye-1 undergoes two reversible one-electron oxidations at 0.36 and 0.63 V for the successive generation of the BDF⁺ radical cation and the BDF²⁺ dication. In contrast, in the case of Dye-2 these processes are not electrochemically fully reversible (see ESI†). This compound shows two distorted anodic peaks with $E^{pa}_1 = 0.51$ V and $E^{pa}_2 = 0.77$ V, and two successive cathodic peaks at $E^{pc}_2 = 0.33$ V and $E^{pc}_3 = 0.43$ V. This observation is indicative of an electron-transfer reaction, most probably coupled with a complex sequence of chemical follow-up processes. Upon the addition of one more cyanoacrylic acid anchoring group, the first oxidation potential is substantially positive-shifted, which reflects the electronic interaction between D and A within these dyes. The first oxidation potential in both cases is more positive than the Co(II)/Co(III) redox couple in use, ensuring efficient regeneration of the oxidized dye. Moreover, the HOMO and LUMO energy levels of both dyes were estimated according to the spectral analyses and the CV data (Table 1). Their relatively low-lying HOMO energy levels are expected to reveal good air stability and a high open circuit voltage ($V_{oc}$) in the DSSC device. Compared to Dye-1, the HOMO and LUMO levels of Dye-2 are energetically lowered due to the strong electron-withdrawing effect of two cyanoacrylic acid anchoring groups.

Density-functional theory (DFT) calculations for both dyes using the Coulomb Attenuated Methods at the B3LYP 6-31G(d,p) level of the theory, support the directional movement of charge upon photoexcitation (for details, see ESI†). As expected, the HOMO and LUMO of Dye-1 and Dye-2 are mainly located on the BDF and 2-cyano-3-(4-ethynylphenyl)acrylic acid moieties, respectively. An energetic stabilization of the HOMO when going from Dye-1 ($\Delta E_{HOMO} = 0.09$ eV) to Dye-2 ($\Delta E_{HOMO} = 0.11$ eV) is predicted, which is in line with the increase of the oxidation potential from Dye-1 to Dye-2; see Table 1.

The electronic spectra of the red colored Dye-1 and Dye-2, recorded in THF solution (see ESI†), show intense optical absorptions over the UV-vis spectral part with absorption onset energies at about 17 900 cm⁻¹ (559 nm) and 17 100 cm⁻¹ (585 nm), respectively. As expected, both of them exhibit a quite similar absorption pattern. Based on the detailed spectral

![Chemical structures of the synthesized dyes.](http://doc.rero.ch)

**Fig. 1** Chemical structures of the synthesized dyes.

![Scheme 1 Synthesis of Dye-1 and Dye-2.](http://doc.rero.ch)
Table 1  Optical and electrochemical data, HOMO and LUMO energy levels, and photovoltaic parameters of Dye-1 and Dye-2 after optimization  

<table>
<thead>
<tr>
<th>Dye</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>( \varepsilon_{\text{max}} ) (10^4 \text{ M}^{-1} \text{ cm}^{-1})</th>
<th>( I_{\text{ph,opt}} ) (eV)</th>
<th>( E^0 ) (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>( J_{\text{sc}} ) (mA cm(^{-2}))</th>
<th>( V_{\text{oc}} ) (mV)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye-1</td>
<td>477 (1.6)</td>
<td>497</td>
<td>2.22</td>
<td>0.36</td>
<td>-5.09</td>
<td>-2.87</td>
<td>8.7</td>
<td>820</td>
<td>0.77</td>
<td>5.5</td>
</tr>
<tr>
<td>Dye-2</td>
<td>516 (2.1)</td>
<td>—</td>
<td>2.12</td>
<td>0.51</td>
<td>-5.11</td>
<td>-2.99</td>
<td>6.1</td>
<td>750</td>
<td>0.81</td>
<td>3.8</td>
</tr>
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</table>

\( a \) Optical band gap is estimated from UV-vis absorption onset. \( b \) The redox potentials vs. Fc+/Fc were recorded in CHCl\(_3\)-Bu\(_4\)NPF\(_6\) (0.1 M) solution. 

Conjugation of the BDF unit. Leakage of electrons from TiO\(_2\) to the electrolyte/the oxidized higher than those for the ICT band in the vacuum level. 

It corresponds to half-wave oxidation potential \( E_{p_{1/2}} \). It corresponds to an anodic peak \( E_{\text{p1}} \). HOMO level is calculated from the onset of the first oxidation potential in cyclic voltammetry, according to the equation \( E_{\text{HOMO}} = [-(E_{\text{onset}} + 4.8)] \text{ eV} \), where 4.8 eV is the energy level of ferrocene below the vacuum level. LUMO level is estimated according to the equation \( E_{\text{LUMO}} = [E_{p_{1/2}} + E_{\text{HOMO}}] \text{ eV} \). The cells were tested with a solution of dye (0.1 mM) in the presence of CDCA using a [Co(n/m)(bpy)]\(_2\) electrolyte under standard air mass 1.5 and simulated sunlight at 1000 W m\(^{-2}\) intensity.

In conclusion, we have presented a new type of dye sensitizers endowed with a BDF \( \pi \)-conducting group for DSSCs, namely, fluorescent Dye-1 and non-emissive Dye-2 with one and two cyanacrylic acid anchoring groups, respectively. For the first time, BDF-sensitized DSSCs are described, showing PCEs of up to 5.5% in the presence of the coabsorbent CDCA. Detailed kinetic studies of DSSCs based on these two dyes will be carried out to determine their quantum yields for electron injection. Also a study on the structural modification of the BDF dyes capable of extending the spectral response to the long wavelength region and further enhancing the DSSC performance, is currently underway.
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Notes and references