Molecular Engineering of a Fluorene Donor for Dye-Sensitized Solar Cells

Aswani Yella,† Robin Humphry-Baker,‡ Basile F. E. Curchod,‡ Negar Ashari Astani,‡ Joël Teuscher,† Lauren E. Polander,† Simon Mathew,‡ Jacques-E. Moser,§ Ivano Tavernelli,‡ Ursula Rothlisberger,‡ Michael Grätzel,† Md. Khaja Nazeeruddin,‡ and Julien Frey*†

†Laboratory of Photonics and Interfaces, ‡Laboratory of Computational Chemistry and Biochemistry, and §Group for Photochemical Dynamics, Institute of Chemical Sciences and Engineering, School of Basic Sciences, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

Supporting Information

ABSTRACT: To improve their efficiency beyond the state-of-the-art, D−π−A dyes must display increased spectral breadth and account for the physical limitations observed in the dye-sensitized solar cells. In particular, they should be designed to control the electron-transfer processes that ensure efficient dye-regeneration and prevent undesired electron recombination. In this article, the electronic and steric properties of a fluorene donor are engineered to meet all these requirements. This elegant donor is featured along with a cyclopentadithiophene bridge and a cyanoacrylic acid acceptor in JF419. A thorough comparison with Y123 and C218 demonstrates the relevance of the design. Relative to conventional donors, the fluorene construct described here enhances the light-harvesting properties, because of its exceptional electron-donating character. The functionalities used to induce the electronic push through the D−π−A structure also provide the dye with favorable steric properties. Indeed, the substitution around the fluorene core adequately insulates the TiO2 surface from the electrolyte, which prevents back-recombination and prolongs the electron lifetime in the semiconductor. Furthermore, compared to analogous dyes, JF419 maintains nearly quantitative regeneration efficiency, despite the lower regeneration driving force. The root of this observation is contributed to a significantly more delocalized hole in the photo-oxidized JF419+, which is highlighted through transient absorption spectroscopy and quantum chemical calculations. The design principles established are relevant to the development of more comprehensive sensitizers, as evidenced by the 10.3% efficiency obtained in cobalt-based liquid dye-sensitized solar cells.

KEYWORDS: solar cells, D−π−A, cobalt electrolyte, structure−property relationship

INTRODUCTION

Solar energy conversion has become a main research topic, in response to growing energy and sustainability concerns. Among the emerging technologies, dye-sensitized solar cells (DSCs) have the potential to compete with conventional silicon solar cells, because of their low-cost manufacturing, great aesthetic features (color, flexibility and transparency), and the potential for indoor and outdoor implementation. A typical DSC is composed of a chromophore that is anchored to a mesostructured, semiconducting TiO2 anode. Upon irradiation, light is absorbed by the sensitizer, which results in electron injection from the photoexcited dye into the conduction band of the semiconductor. Subsequently, the oxidized form of the dye is regenerated by electron donation from a redox shuttle. The electrons flow from the photoanode to the counter electrode, where the mediator is, in turn, reduced. Under a given incident illumination intensity P,in, the power conversion efficiency of a cell (η) is defined as the product of the generated photocurrent density (JSC), the open-circuit potential (VOC), and the fill factor (FF), as follows:

\[
\eta = \frac{J_{SC} \times V_{OC} \times FF}{P_{in}}
\]

In donor−bridge−acceptor (D−π−A) organic sensitizers, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are spatially differentiated. The HOMO resides preferentially across the donor and the bridge, whereas the LUMO extends predominantly across the bridge and the acceptor. Because of intrinsic electron-donating properties, triphenylamines are frequently used as donors.2 The choice of donor affects the intramolecular charge transfer (ICT) within the dye, both in wavelength and...
intensity of the absorption band. Stronger electron donation is expected to reduce the optical gap and produce a red-shift in absorption by raising the HOMO energy level more than that of the LUMO.

From a device point of view, the donor also dictates the oxidation potential of the redox mediator that performs the regeneration of the oxidized dye. Furthermore, the donor provides a means to engineer the interface between the dye–
TiO2 layer and the electrolyte. This aspect is critical when cobalt complexes are used as redox mediators. Until recently, DSCs using cobalt shuttles were limited in efficiency due to rapid recombination of electrons from the conduction band of TiO2 to the cobalt(III) species, slow dye regeneration, and mass-transport limitations within the mesoporous electrode. In 2010, Feldt et al. demonstrated that the presence of bulky substituents on triarylamine-based donors considerably enhances the performance in DSCs by preventing the redox mediator to access to the TiO2 surface. As a result of this physical insulation (also referred to as umbrella effect), electron lifetime in the semiconductor can be significantly prolonged, which improves the photocurrent and photovoltage. In addition, the steric properties of the donor can limit aggregation between the dye molecules, which is a recurrent problem during device fabrication and operation.

Favorable electron-donating and steric properties of the donor have been explored for C218 and Y123, respectively. Interestingly, both dyes revolve around the 4H-cyclopenta[2,1-b:3,4-b′]dithiophene (labeled CPDT) bridge and the cyanoacrylic acid acceptor. We describe herein a new sensitizer (JF419) that emulates the strong electronic push of C218 and the favorable back-recombination features of Y123, all with a single donor (see Figure 1). The desired effect is obtained using a fluorene moiety without further modification at the π-bridge or the acceptor. The synthesis of this sensitizer is detailed in the Supporting Information (Scheme S1). Because of this careful design, DSCs based on JF419 achieve efficiencies up to 11.1% at 50% sun, and 10.3% overall efficiency at AM 1.5 G simulated sunlight (100 mW cm−2, i.e., full sun) in presence of a standard cobalt electrolyte. Changes in photoelectrochemical properties and device efficiencies are discussed based on modifications at the donor side and compared to reference dyes outlined above. The present work provides a comprehensive structure–property relationship for the design of future fluorene donors, which remains inconsistent in the literature.

### RESULTS AND DISCUSSION

The optical properties of Y123, C218, and JF419 were measured in dichloromethane and acetonitrile solutions. The shape of the absorption and emission spectra are strongly dependent on the solvent, as shown in the Supporting Information. A series of excitation spectra indicates the presence of two species that are linked to the protonation state of the cyanoacrylic acceptor. The ratio between the protonated and deprotonated form of the dye varies with solvent polarity. In nonpolar solvents such as dichloromethane (Figure 2a), the acid–base equilibrium is displaced toward the acidic form of the dye. In contrast, in polar solvents such as acetonitrile, the equilibrium is shifted toward the conjugate base. Solutions containing only one form of the dye can be obtained by adjusting the pH through the addition of small amount of acetic acid or triethylamine. Absorption and emission spectra of the acidic and basic forms of Y123, C218, and JF419 are compared in the Supporting Information (see Figure S9 and Table S1). In pure dichloromethane, the ICT band maximum is observed at 542, 549, and 554 nm, respectively, with similar extinction coefficients.
donating alkoxy groups\textsuperscript{20} in para position to the amine. This substitution pattern sets the oxidation potential of the dye at +0.93 V vs NHE,\textsuperscript{21} in agreement with potentials recorded for related triphenylamines.\textsuperscript{22} This donor induces a strong electronic push within the D–π–A system of the dye and provides C218 with a large absorption over the visible spectrum, as shown in Figure 2b. In contrast, the donor used in Y123 is naturally twisted at the biphenyl moieties (see Figure 7, presented later in this work), and the electron-donating groups are only weakly conjugated with the central triphenylamine core. As a result, the oxidation potential of the dye is measured 80 mV higher than for C218 ($E_{S+/S} = +1.01$ V). In accordance, the absorption maximum of Y123 blue-shifts from 445 nm to 441 nm.

In principle, a shift of the ICT band toward higher energy wavelengths is detrimental to the device efficiency, because it reduces the harvesting of lower-energy photons.\textsuperscript{18} The lack of long-wavelength absorption of Y123 can be resolved by modifying the structure of the donor. We reasoned that a fluorene donor would bring the electron-donating alkoxy groups in conjunction with the central amine, thereby enhancing electronic push through the D–π–A system. Planarization of the donor results in drastic changes of the optical and electrochemical properties of the dye. First, JF419 experiences a 150 and 70 mV negative shift in oxidation potential, compared to Y123 and C218, respectively. This positions the HOMO energy level at $-4.97$ eV vs the vacuum level.\textsuperscript{23} Second, the absorption maximum is measured at 468 nm for the TiO$_2$ film, which corresponds to a 25-nm redshift, compared to Y123. As expected, the $E_{0-\alpha}$ values measured at the intersection of the absorption and the normalized emission of the films are progressively reduced with increasing electron-donating strength from the donor. The $E_{0-\alpha}$ optical gap sets the first excited state oxidation potential ($E_{S+/S^*}$) of each dye at much higher energy than the TiO$_2$ conduction band ($E_C \approx -3.60$ eV vs vacuum level),\textsuperscript{24} thus providing ample driving force for injection.

All the aforementioned properties of JF419 are reflected in the theoretical calculations (DFT/M06/SMD(CH$_2$Cl$_2$) for geometry optimization\textsuperscript{25–27} and LR-TDDFT/BMK/SMD(CH$_2$Cl$_2$) for excitation energies\textsuperscript{28} see the Supporting Information for full details). The strong transition from the ground state ($S_0$) to the first excited electronic state $S_1$ is computed at 2.27 eV (exp: 2.24 eV), a value that has been redshifted, compared to the first transition of C218 at 2.30 eV (exp: 2.26 eV) or Y123 at 2.32 eV (exp: 2.29 eV). The strong Kohn–Sham (KS) HOMO to LUMO contribution (81.5%; see Figure 3, left) computed for the $S_0 \rightarrow S_1$ excitation supports a strong donor-to-acceptor transition. This character is further validated by the analysis of the corresponding natural transition orbitals (Figure 3, right). Both the vertical and the adiabatic ionization energies\textsuperscript{29} were computed for the three different compounds at the (U)DFT/M06 level of theory. JF419 is found to have the lowest ionization energy (vertical: 4.76 eV, adiabatic: 4.67 eV), followed closely by C218 (vertical: 4.86 eV, adiabatic: 4.73 eV) and finally Y123 (vertical: 4.91 eV, adiabatic: 4.83 eV), which is a general trend that follows the reported experimental results and further highlights the strength of the fluorene donor.

The photovoltaic properties of JF419 were compared to Y123 and C218 in a series of dye-sensitized solar cells containing a mixture of cobalt(II/III)-tris(bipyridyl) complexes—[$\text{Co}^{II/III}(\text{bpy})_3]^{2+/3+}$—as a redox mediator. The bis(trifluoromethane)sulfonimide salt (TFSI) was preferred to improve solubility in acetonitrile. The Co$^0$ and Co$^{II}$ complexes were mixed in a 0.25:0.06 molar ratio, respectively. Given that the experimental standard potential of the [$\text{Co}^{II/III}(\text{bpy})_3]^{2+/3+}$ couple is measured +0.57 V vs NHE,\textsuperscript{12} using the Nernst equation, the oxidation potential of the electrolyte used here is derived at +0.54 V vs NHE. The electrolyte also contains LiTFSI and 4-tert-butylpyridine (TBP), whose concentrations influence the device performance, as shown in Figure 4. Li$^+$ ions and TBP have opposite effects on the conduction band and trap states, and, thus, on the kinetics of electron injection and recombination.\textsuperscript{18} Nevertheless, optimization of their concentration leads to a compromise where the position of the conduction band favors efficient electron injection while maintaining high photovoltage. In this study, in addition of [$\text{Co}^{II/III}(\text{bpy})_3]^{2+/3+}$, the electrolyte also contains 0.25 M tert-butylpyridine, along with 0.1 M LiTFSI in acetonitrile as a solvent, a composition that maximizes the photocurrent. The final section of the present work examines conditions (1.0 M TBP and 0.1 M LiTFSI) where the photovoltage is maximized.

Figure 5a shows the incident photon-to-current conversion efficiency (IPCE), as a function of the light excitation wavelength for DSCs with this optimized electrolyte. Films

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**Table 1. Optical and Electrochemical Data in Solution and on TiO$_2$ Films for Y123, C218, and JF419**

<table>
<thead>
<tr>
<th>dye</th>
<th>$\lambda_{max}$ (nm)</th>
<th>$\epsilon$ (M$^{-1}$ cm$^{-1}$)</th>
<th>$E_{S+/S}$ (V)</th>
<th>$E_{HOMO}$ (eV)</th>
<th>$E_{PL}$ (nm)</th>
<th>$E_{0-\alpha}$ (eV)</th>
<th>$E_{S+/S}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y123</td>
<td>542</td>
<td>50500</td>
<td>1.01</td>
<td>$-5.08$</td>
<td>441</td>
<td>672</td>
<td>2.17</td>
</tr>
<tr>
<td>C218</td>
<td>549</td>
<td>46000</td>
<td>0.93</td>
<td>$-4.99$</td>
<td>445</td>
<td>673</td>
<td>2.13</td>
</tr>
<tr>
<td>JF419</td>
<td>554</td>
<td>47500</td>
<td>0.85</td>
<td>$-4.92$</td>
<td>468</td>
<td>708</td>
<td>2.10</td>
</tr>
</tbody>
</table>

*Measured with 0.1 M Bu$_4$NPF$_6$ in DMF, using a scan rate of 1000 mV s$^{-1}$; potentials are given in V vs NHE. \textsuperscript{2}Calculated vs vacuum level according to the formula $E_{HOMO} = -(4.75 + E_{S+/S} - E_{(Fcs/Fc)})$, with $E_{(Fcs/Fc)} = +0.69$ V vs NHE in DMF. \textsuperscript{3}Measured on a 3.3-μm-thick TiO$_2$ film. \textsuperscript{4}Excitation at 460 nm. \textsuperscript{5}Measured at the intersection of normalized absorption and emission of the TiO$_2$ films. \textsuperscript{6}Calculated according to the following formula: $E_{S+/S} = E_{HOMO} + E_{0-\alpha}$.\textsuperscript{7}presented later in this work, and the electron-donating alkoxy groups are only weakly conjugated with the central triphenylamine core. As a result, the oxidation potential of the dye is measured 80 mV higher than for C218 ($E_{S+/S} = +1.01$ V). In accordance, the absorption maximum of Y123 blue-shifts from 445 nm to 441 nm.
The electrolyte contains a mixture of 0.25 M [Co(bpy)3]2(TFSI)2 and 0.06 M [Co(bpy)3]2(TFSI)3 as a redox mediator.

Decays in acetonitrile (e) and in the presence of [CoII/III(bpy)3]2/3+ electrolyte (f). Laser pulse < 40 μJ cm−2.

The solar-to-electricity conversion efficiency for current generation is close to unity when taking into account light reection by the glass. This is significantly better than Y123 and C218 films for which <75% of the incident light is converted from 400 nm to 620 nm. Furthermore, the IPCE spectrum of JF419 is drastically higher at longer wavelength, with slow decline until 740 nm.

The solar-to-electricity conversion efficiencies were evaluated by recording the J−V characteristics measured under simulated AM 1.5 G simulated sunlight (100 mW cm−2) for devices employing Y123, C218, and JF419. Film thickness: 4.0 ± 0.4 μm. Electrolyte: 0.25 M [Co(bpy)3]2(TFSI)2, 0.06 M [Co(bpy)3]2(TFSI)3, 0.25 M TBP, 0.1 M LiTFSI in acetonitrile.

Table 2. Photovoltaic Parameters of Devices Employing Y123, C218, and JF419 under Simulated AM 1.5 G Full Sun Illumination (100 mW cm−2)

<table>
<thead>
<tr>
<th>dye</th>
<th>Jsc (mA cm−2)</th>
<th>Voc (mV)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y123</td>
<td>14.1</td>
<td>876</td>
<td>0.78</td>
<td>9.8</td>
</tr>
<tr>
<td>C218</td>
<td>14.8</td>
<td>755</td>
<td>0.77</td>
<td>8.6</td>
</tr>
<tr>
<td>JF419*</td>
<td>16.2 (16.2 ± 0.6)</td>
<td>840 (830 ± 13)</td>
<td>0.76 (0.76 ± 0.01)</td>
<td>10.3 (10.1 ± 0.2)</td>
</tr>
</tbody>
</table>

*Average values are based on three replicate measurements.

Figure 5. (a) Photocurrent action spectra and (b) J−V characteristics measured under simulated AM 1.5 G simulated sunlight (100 mW cm−2) for devices employing Y123, C218, and JF419. Film thickness: 4.0 ± 0.4 μm. Electrolyte: 0.25 M [Co(bpy)3]2(TFSI)2, 0.06 M [Co(bpy)3]2(TFSI)3, 0.25 M TBP, 0.1 M LiTFSI in acetonitrile.

Figure 4. (a) TBP and (b) LiTFSI concentration dependence of photovoltage and photocurrent for films sensitized with JF419. The electrolyte contains a mixture of 0.25 M [Co(bpy)3]2(TFSI)2 and 0.06 M [Co(bpy)3]2(TFSI)3 as a redox mediator.

Figure 6. (a, b, c) Photoinduced absorption (PIA) spectra in acetonitrile after 470 nm excitation, and (d, e, f) corresponding TA decay traces following excitation at 530 nm (probe at 750 nm) of 8.0-μm-thick TiO2 films coated with Y123, C218, and JF419, respectively.

The IPCE intensity is a function of charge collection, electron injection in the TiO2, and dye regeneration. We used single-photon counting techniques to examine the influence of the LUMO energy level upon the quantum yield of electron injection from the excited state of the dye to the TiO2.30,31 For Y123, C218, and JF419, quantitative electron injection yields were measured, which indicates that exciton dissociation is not a key determinant. To further rationalize the IPCE intensities, we performed transient absorption (TA) measurements and estimated the time constants of charge recombination and dye regeneration. The oxidized forms of the dyes have absorption spectra that sharply contrast with their neutral counterparts, as shown in Figures 6a–c. Following excitation at 470 nm, signals that appear below 650 nm and within 650–850 nm are characteristic of the ICT band bleaching and TA of triphenylamine radicals, respectively. Time constants are derived from TA decays of the corresponding radical. The signals were fitted with a single exponential component decay, ∆A(t) ∝ A0 exp[−(t/τ)], where A0 is a pre-exponential factor and τ is the characteristic time.32 The fits are represented as solid lines in Figures 6d–f, with data reported in Table 3.

In the absence of electrolyte (dummy cells in acetonitrile), the time constants τrec for the recombination of electrons in the TiO2 with the oxidized form of the dye are on the same order of magnitude for the three dyes. The lower τrec value measured for JF419 suggests that charges could recombine slightly faster when the fluorene donor is used. In the presence of
There is no discernible image.
Figure 9. J–V characteristics measured for devices employing JF419 under 10%, 50%, 64%, and 100% AM 1.5 G simulated sunlight (100 mW cm⁻²) with (a) 0.25 M TBP and (b) 1.0 M TBP. Film thickness: 4.0 ± 0.5 μm. Electrolyte: 0.25 M [Co(bpy)₃][TFSI]₂, 0.06 M [Co(bpy)₃][TFSI]₀, 0.1 M LiTFSI in acetonitrile.

Table 4. Detailed Photovoltaic Parameters of Our Record Devices Employing JF419 with 0.25 or 1.0 M TBP.

| Containing Electrolyte at Different Incident Light Intensities P₀,0 Incident Intensity of AM 1.5 G Simulated Sunlight |
|--------------------|------------------|------------------|------------------|------------------|------------------|
| [TBP] | P₀,0 (mW cm⁻²) | J_SC (mA cm⁻²) | V_OC (mV) | FF | η (%) |
| 0.25 M | 9.5 | 1.6 | 754 | 0.78 | 9.9 |
| 0.25 M | 51.5 | 8.5 | 815 | 0.77 | 10.4 |
| 0.25 M | 64.9 | 10.6 | 823 | 0.77 | 10.4 |
| 0.25 M | 100.1 | 16.2 | 840 | 0.76 | 10.3 |
| 1.0 M | 9.3 | 1.6 | 829 | 0.78 | 11.1 |
| 1.0 M | 49.9 | 8.3 | 887 | 0.75 | 11.1 |
| 1.0 M | 63.2 | 10.2 | 893 | 0.74 | 10.7 |
| 1.0 M | 97.8 | 12.6 | 904 | 0.78 | 9.0 |

threshold. This is a remarkable result considering the number of new sensitizers that have been developed in recent years, particularly CPDT derivatives. However, this performance is not sustained above 50%-sun illumination, because of a drop in efficiency at the counter electrode, which could be addressed using more catalytically active electrodes than platinum.

**CONCLUSION**

The fluorene donor described here is an excellent example of how comprehensive structure–property–performance relationships can help to design novel sensitizers for use in dye-sensitized solar cell (DSC) applications. In this work, we merged two established concepts, strong electron donation and merged two established concepts, strong electron donation and surface insulation, while taking into account the intrinsic limitations of the device. The resulting JF419 sensitizer shows superior incident photon-to-current conversion efficiency (IPCE) response and efficiencies than previous organic dyes, demonstrating the relevance of the design.

**ASSOCIATED CONTENT**

Supporting Information

Synthetic procedures and characterizing data for experimentally studied compounds; details of quantum-chemical calculations and device studies; supplemental figures discussed in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: julien.frey@gmail.com.*

Notes

The authors declare no competing financial interest.

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19. The conduction band edge of the TiO₂ semiconductor shows Nernstian dependence on pH, see: Bolts, J. M.; Whitton, M. S. J. Phys. Chem. 1976, 80, 2641–2645. Our best-performing films are obtained when dyes are adsorbed from a 1:4 mixture of tetrahydrofuran and ethanol, in which the deprotonated form prevails.
(29) The vertical ionization corresponds to the energy difference between the cationic and the neutral species at the molecular geometry of the neutral compound; the adiabatic ionization energy corresponds to the energy difference between the optimized cationic and optimized neutral species.