Supporting Information for:

Carboxypyridinium Isomers as Anchoring Groups for Dye-Sensitized Solar Cells: Influence of Structure on Photochemical Properties

Daniele Franchi, Massimo Calamante, Gianna Reginato, Lorenzo Zani, Maurizio Peruzzini, Maurizio Taddei, Fabrizia Fabrizi de Biani, Riccardo Basosi, Adalgisa Sinicropi, Daniele Colonna, Aldo Di Carlo, Alessandro Mordini

a Università degli Studi di Firenze, Dipartimento di Chimica “Ugo Schiff”, Via della Lastruccia 13, 50019 Sesto Fiorentino, Italy. b CNR-Istituto di Chimica dei Composti Organometallici (CNR-ICCOM), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy. c Università degli Studi di Siena, Dipartimento di Biotecnologie, Chimica e Farmacia, Via A. Moro 2, 53100 Siena, Italy. d Consorzio Dyepower, Viale Castro Pretorio 122, 00185 Roma, Italy. e Centre for Hybrid and Organic Solar Energy (CHOOSE), Dipartimento di Ingegneria Elettronica, Universita di Roma Tor Vergata, Via del Politecnico 1, 00133 Roma, Italy.

Email: alessandro.mordini@iccom.cnr.it
1. Computational details

DFT calculations were performed with the Gaussian 09 program package. Geometry optimization was carried out \textit{in vacuo} using the B3LYP functional and the standard 6-31G* basis set for all atoms. The absorption maximum ($\lambda_{\text{max}}$), vertical excitation energy ($E_{\text{exc}}$), and oscillator strength ($f$) in CH$_2$Cl$_2$ solution were calculated on the optimized structures via time-dependent DFT (TD-DFT) at the CAMB3LYP 6-31G* and MPW1K/6-31G* levels. Solvent effects were included by using the polarizable continuum model (PCM).

\textbf{Figure S1.} Wave function plots, orbital energies and frontier orbital energy gaps of compounds DF13A,C and DF39A,C.
Table S1. CAMB3LYP/6-31G* and MPW1K/6-31G* absorption maxima ($\lambda_{\text{max}}$), oscillator strengths (f), vertical excitation energies ($E_{\text{exc}}$) and main electronic transitions for dyes DF39A,C in CH$_2$Cl$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Functional</th>
<th>$\lambda_{\text{max}}$ [nm]</th>
<th>f</th>
<th>$E_{\text{exc}}$ [eV]</th>
<th>Main transition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DF39A</td>
<td>CAMB3LYP</td>
<td>498</td>
<td>1.68</td>
<td>2.49</td>
<td>H $\rightarrow$ L</td>
</tr>
<tr>
<td></td>
<td>MPW1K</td>
<td>536</td>
<td>1.53</td>
<td>2.31</td>
<td>H $\rightarrow$ L</td>
</tr>
<tr>
<td></td>
<td></td>
<td>experimental:</td>
<td>496</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td>DF39C</td>
<td>CAMB3LYP</td>
<td>513</td>
<td>1.69</td>
<td>2.42</td>
<td>H $\rightarrow$ L</td>
</tr>
<tr>
<td></td>
<td>MPW1K</td>
<td>554</td>
<td>1.53</td>
<td>2.24</td>
<td>H $\rightarrow$ L</td>
</tr>
<tr>
<td></td>
<td></td>
<td>experimental:</td>
<td>520</td>
<td>2.38</td>
<td></td>
</tr>
</tbody>
</table>

2. Synthetic procedures

2.1. General Remarks

All reactions were performed under an inert nitrogen atmosphere in a flame- or oven-dried apparatus, using Schlenk techniques. Tetrahydrofuran (THF) was purified by distillation over metallic sodium in the presence of benzophenone, toluene was distilled over metallic sodium. Methanol, CH$_2$Cl$_2$, and N,N-dimethylformamide were dried by storing under nitrogen over 4 Å molecular sieves. Carboxypyridines (DF13A, DF13C) were prepared according to our published procedure. All other chemicals employed were commercially available and used as received. Petroleum ether was the 40-60 °C boiling fraction. Thin layer chromatography was carried out on aluminum-supported Merck 60 F254 plates; detection was carried out using UV light and permanganate solutions followed by heating. Flash column chromatography was performed using Merck Kieselgel 60 (300-400 mesh) as the stationary phase. $^1$H-NMR spectra were recorded at 200, 300 or 400 MHz, and $^{13}$C-NMR{$^1$H} spectra were recorded at 50.3, 75.5 or 100.6 MHz. Chemical shifts were referenced to the residual solvent peak (CHCl$_3$, δ 7.26 ppm for $^1$H-NMR and δ 77.16 ppm for $^{13}$C-NMR; DMSO-$d_6$, δ 2.50 ppm for $^1$H-NMR). FT-IR spectra were recorded in the range 4000 – 400 cm$^{-1}$ with a 2 cm$^{-1}$ resolution. ESI-MS spectra were obtained by direct injection of the sample solution, using a Thermo Scientific LCQ-FLEET instrument and are reported in the form m/z. HRMS spectra were measured using a Thermo Scientific LTQ Orbitrap (FT-MS) instrument.
2.2. Protection of carboxypyridines: general procedure

The appropriate carboxypyridine DF13A,C (253 mg, 0.37 mmol) was dissolved in dry dichloromethane (2 mL) and then oxalyl chloride (38 µL, 0.45 mmol, 1.2 eq.) was added, giving rise to a blue solution. One drop of DMF was added and evolution of gas was observed. After 10 minutes allyl alcohol (128 µL, 1.88 mmol, 5.0 eq.) was added. The reaction mixture was left under stirring for an hour, then quenched with aq. phosphate buffer (pH 7.5) and extracted with ethyl acetate (10 mL). The red organic phase was washed with water (2 × 5 mL) and brine (5 mL), then dried on Na₂SO₄. The solvent was removed under reduced pressure and the crude product purified by flash chromatography.

2.2.1. (E)-Allyl 6-(5-(4-(bis(4-(hexyloxy)phenyl)amino)styryl)thio-phen-2-yl)nicotinate (1a)
(Petroleum ether / ethyl acetate, gradient = 50:1 to 5:1). 50 mg, 70% yield. Red amorphous solid.  

**1a:** ¹H-NMR (200 MHz, CDCl₃) δH 9.17 (1H, d, J = 1.8 Hz), 8.25 (1H, dd, J = 8.4, 2.2 Hz), 7.65 (1H, d, J = 8.4 Hz), 7.56 (1H, d, J = 4.0 Hz), 7.28 (2H, d, J = 8.4 Hz), 6.78 - 7.14 (13H, m), 5.93 - 6.16 (1H, m), 5.44 (1H, dd, J = 17.2, 1.5 Hz), 5.33 (1H, d, J = 11.4 Hz), 4.86 (2H, d, J = 5.5 Hz), 3.94 (4H, t, J = 6.6 Hz), 1.68 - 1.88 (4H, m), 1.29 - 1.58 (12H, m), 0.93 (6H, t, J = 6.2 Hz) ppm. ¹³C-NMR{¹H} (100 MHz, CDCl₃) δC 164.5, 155.7, 151.1, 148.8, 147.7, 140.9, 140.2, 137.5, 131.9, 130.1, 128.3, 127.9, 127.3, 127.2, 126.8, 126.3, 123.2, 113.9, 118.6, 118.5, 117.6, 115.2, 68.2, 65.7, 31.6, 29.3, 25.7, 22.6, 14.0 ppm; IR (KBr) cm⁻¹ 3046, 2852, 1715, 1591. MS (ESI) m/z calced for C₄₅H₅₀N₂O₄S: 714.3. Found: 715.4 [M+1]⁺.

2.2.2. (E)-Allyl 4-(5-(4-(bis(4-(hexyloxy)phenyl)amino)styryl)thio-phen-2-yl)picolinate (1b)
(Petroleum ether/Ethyl Acetate, gradient = 50:1 to 5:1). 73 mg, 46% yield. Red-orange amorphous solid.  

**1b:** ¹H-NMR (400 MHz, CDCl₃) δH 8.68 (1H, d, J = 5.2 Hz), 8.29 (1H, d, J = 1.3 Hz), 7.57 (1H, dd, J = 5.2, 1.3 Hz), 7.47 (1H, d, J = 3.7 Hz), 7.28 (2H, d, J = 8.4 Hz), 7.11-6.79 (13H, m), 6.21-6.01 (1H, m), 5.46 (1H, dd, J = 17.0, 0.9 Hz), 5.34 (1H, dd, J = 10.3, 0.9 Hz), 4.94 (2H, d, J = 5.9 Hz), 3.93 (4H, t, J = 6.4 Hz), 1.87-1.68 (4H, m), 1.51-1.31 (12H, m), 0.92 (6H, t, J = 6.2 Hz) ppm. ¹³C-NMR{¹H} (100 MHz, CDCl₃) δC 164.5, 155.4, 150.0, 148.6, 148.2, 146.2, 142.3, 139.8, 138.4, 136.8, 131.4, 129.9, 127.7, 127.0, 126.6, 126.1, 121.7, 120.4, 119.5, 119.0, 117.8, 115.0, 68.1, 66.6, 31.6, 29.3, 25.7, 22.6, 14.0 ppm. IR (KBr) cm⁻¹ 3041, 2953, 1735, 1589. MS (ESI) m/z calced for C₄₅H₅₀N₂O₄S: 714.3. Found: 715.3 [M+1]⁺.
2.3. Synthesis of (E)-5-(Allyloxycarbonyl)-2-(5-(4-(bis(4-(hexyloxy)phenyl)amino)styryl)thiophen-2-yl)-1-methylpyridinium tetrafluoborate (2a)

Ester 1a (40 mg, 0.06 mmol, 1.0 eq.) was dissolved in dry CH₂Cl₂ (1 mL), the solution was cooled at 0°C, then Cs₂CO₃ (73 mg, 0.22 mmol, 4.0 eq.) and trimethyloxonium tetrafluoroborate (Me₃OBF₄, 24 mg, 0.16 mmol, 3.0 eq.) were added. The solution was stirred at 0°C for 15 minutes, then warmed to room temperature and left under stirring overnight. The reaction mixture was diluted with dichloromethane (10 mL), the organic phase was washed with a cold saturated solution of NH₄Cl (10 mL) and the aqueous solution extracted with dichloromethane (2 × 10 mL). The combined organic phases were dried on Na₂SO₄. The solvent was removed under reduced pressure and the crude product purified by flash column chromatography (CH₂Cl₂/MeOH/formic acid 10:1:0.1). A red-violet amorphous solid was recovered (37 mg, 0.05 mmol, yield 85%).

(2a): ¹H-NMR(200 MHz, CDCl₃) δH 9.27 (1H, brs), 8.70 (1H, d, J = 7.0 Hz), 8.07 (1H, d, J = 7.0 Hz), 7.79 (1H, brs), 7.44-6.94 (9H, m), 6.94-6.53 (6H, m), 6.20-5.78 (1H, m), 5.65-5.22 (2H, m), 4.87 (2H, d, J = 4.4 Hz), 4.57 (3H, br s), 3.93 (4H, t, J = 12.5 Hz), 1.95-1.62 (4H, m), 1.56-1.07 (12H, m), 0.91 (6H, t, J = 5.5 Hz) ppm. ¹³C-NMR{¹H} (100 MHz, CDCl₃) δC ppm 161.4, 156.4, 154.2, 152.4, 150.0, 143.6, 140.0, 137.6, 134.2, 131.2, 129.6, 128.4, 127.5, 127.3, 127.2, 127.1, 126.8, 120.5, 119.5, 116.6, 115.7, 68.6, 67.9, 49.4, 31.9, 29.6, 26.1, 23.0, 14.4 ppm. IR (KBr) cm⁻¹ 3056, 2987, 1735, 1635, 1627, 1593. MS (ESI) m/z calc'd for C₄₆H₅₃N₂O₄S: 729.4. Found: 729.4 [M]+
3. UV-Vis and Fluorescence Spectroscopy

UV-Vis spectra were recorded with a Varian Cary 400 spectrometer, fluorescence spectra were recorded with a Varian Eclipse instrument, irradiating the sample at the wavelength corresponding to maximum absorption in the UV spectrum.

![Normalized UV-Vis absorption (solid symbols) and fluorescence emission (hollow symbols) spectra of compounds DF39A and DF39C in EtOH solution. DF39A: black squares; DF39C: red circles.](image)

**Fig. S2.** Normalized UV-Vis absorption (solid symbols) and fluorescence emission (hollow symbols) spectra of compounds DF39A and DF39C in EtOH solution. DF39A: black squares; DF39C: red circles.

4. Electrochemical measurements

Electrochemical measurements were carried out in commercially available anhydrous 99.9%, HPLC grade CH₂Cl₂ for electrochemistry. The supporting electrolyte used was electrochemical grade [N(Bu)₄]PF₆. Cyclic voltammetry was performed in a three electrode C-3 BAS Cell having a glassy carbon working electrode, a platinum counter electrode, and the aqueous Ag/AgCl NaCl (3 M) reference electrode. A BAS 100A electrochemical analyzer was used as a polarizing unit. Under these experimental conditions, the one electron oxidation of ferrocene occurs at $E^0 = 0.42$ V.
5. Fabrication and measurement of dye-sensitized solar cells

The titania paste used for the strip cells (Dyesol 18NR-T) was screen-printed on an 8 Ω/sq conductive glass substrate (Pilkington), and the resulting electrodes (active area: 3.6 cm$^2$) were sintered at 520 °C for 30 min. After sintering, the thickness of the layers was measured by means of a profiler (Dektak 150, Veeco). Counter electrodes (CE) were obtained by screen printing a platinum-containing paste on glass substrates (Chimet) and were processed at 420 °C for 15 min. Titania photo-electrodes were sensitized by overnight immersion at rt into the appropriate dye solution (2.0 × 10$^{-4}$ M in EtOH). After sensitization, the photoanodes were rinsed with EtOH and deionized water, dried and joined to the CEs with a 60 μm Bynel® gasket (Solaronix). The internal space of the cells was filled with a triiodide/iodide-containing high stability electrolyte (HSE, Dyesol) by vacuum backfilling through a hole previously drilled in the CE, which was finally closed by using additional sealing film and a small glass cover.

The devices underwent photovoltaic characterization by using an AM 1.5G solar simulator equipped with a Xenon lamp (KHS Solar Constant 1200). The measurements were performed with a power of incoming radiation of 100 mW/cm$^2$. $J/V$ curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source-meter, under the control of dedicated LabTracer 2.0 software. A black shading mask was used to avoid overestimation of the measured parameters. IPCE spectra were measured with a dedicated apparatus built with the following components: Newport model 70 612 Xenon lamp (150 W), Cornerstone 130 1/8 m monochromator and Keithley model 2400 digital source-meter.

Fig. S3. Cyclic Voltammetry plots relative to compounds DF39A and DF39C.
**Fig S4.** IPCE spectra for the different cells built with dye **DF39A**. Cells w/o CDCA: full symbols; cells with CDCA: hollow symbols. 3 μm thickness: black squares; 6 μm thickness: blue triangles.

6. **ESI-MS study of the decomposition product of DF39C**

**Fig S5.** ESI-MS spectrum of the sample obtained by filtration of the **DF39C**/TiO$_2$ slurry after irradiation for 24 h in acetonitrile/aqueous ammonia.
Copies of $^1$H-and $^{13}$C-NMR spectra of compounds 1a, 1b, DF39A, DF39C.

$^1$H NMR of compound 1a

$^{13}$C NMR of compound 1a
$^1$H NMR of compound 1b

$^{13}$C NMR of compound 1b

$^1$H NMR of compound DF39A
$^{13}$C NMR of compound **DF39A**

$^1$H NMR of compound **DF39C**
$^1$H NMR of compound DF39C

References


