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Supporting Information

**New D-π-A-conjugated metal-free organic sensitizers based on alpha -pyranylidene donors for dye-sensitized solar cells**

Emilie Ferreiraa, Pascal Le Poula, Nolwenn Cabona, Bertrand Caroa, Françoise Robin-Le Guena,[[1]](#footnote-1)\*,Yann Pellegrinb, Aurélien Planchatb and Fabrice Odobelb

a Institut des Sciences Chimiques de Rennes UMR CNRS 6226, IUT de Lannion, Rue Edouard Branly, BP 30219, F22302 Lannion Cedex, France

*bUniversité LUNAM, Université de Nantes, CNRS, Chimie et Interdisciplinarité: Synthèse, Analyse, Modélisation (CEISAM), UMR 6230, 2 rue de la Houssinière, 44322 Nantes Cedex 3, France*

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General experimental information

**General experimental details**

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk-line Techniques. Infrared-spectra were recorded on a Perkin-Elmer spectrum1000 FTIR using KBr plates.

All NMR data are reported in ppm (δ) relative to tetramethylsilane as external reference. Coupling constants are reported in Hz. 1H and 13C NMR Spectra were recorded at room temperature in CDCl3, DMSO-*d6* or acetone-*d6* on a Bruker DRX 500 spectrometer and a Bruker Advance 300 spectrometer at the “Institut Universitaire de Technologie de Lannion”. Mass spectra were performed at the "Centre Régional de Mesures Physiques de l’Ouest" (CRMPO, University of Rennes). Mass spectra were obtained with a high resolution MS/MS Zab specra Tof micromass. UV-vis absorption spectra were recorded on a UV-vis Perkin Elmer spectrophotometer lambda 25. Cyclic voltammetry experiments were performed with a µ-AUTOLAB III potentiostat monitored by the GPES software (Metrohm). The redox properties were measured in CH2Cl2-[Bu4N][PF6]. The working electrode was a glassy carbon disk and the counter electrode was a tungsten wire. A non-aqueous Ag+/Ag electrode was used as reference and ferrocene standard was added at the end of each experiment. The redox potential of the ferrocenium-ferrocene couple in CH2Cl2/NBu4PF6 was measured experimentally with reference to the standard calomel electrode (SCE): E1/2(Fc+/Fc) = 0.41 V vs. SCE, and recalibrated vs. NHE assuming that E0(SCE) = 0.24 V vs. NHE.

Synthetic procedures and Spectroscopic Data

**Synthetic procedures**

*Synthesis of aldehydes* ***7*** *and* ***9***

Aldehydes were obtained from a hydrolysis reaction of the corresponding imminium salts which were synthetized in acetic anhydride from the chalcogenopyrylium salts and N,N-dimethylaminoacrolein. (G. A. Reynolds, J. A. VanAllan, *J.Org. Chem.*, **1969**, *34*, 2736)

*Synthesis of aldehyde* ***7***:

1.5g (2.93mmol) of the imminium salt were added to a 50/50 mixture of diethyl ether and 2% aqueous solution of NaOH. The heterogenous mixture was stirred during one night at room temperature. The product was then extracted with diethyl ether and washed three times with water. After evaporation of the solvent the crude product was filtered on silicagel with diethyl ether as eluent. Evaporation of the solvent lead to aldehyde 7 as a black powder (m = 0.9g ; 78%).

*Synthesis of aldehyde* ***9***:

The same procedure was used from 1.22g (2.31 mmol) of the corresponding imminium salt. Aldehyde **9** was obtained as a black powder (m = 0.8g ; 84%).

*Synthesis of dyes (compounds* ***10*** *to* ***18****)*

These compounds were obtained using the same procedure as depicted, for compound **15**. TLC of the reaction mixture was used to determine the best time duration of the reactions. Optimized temperatures were also determined for each compound. For each reaction, decarboxylation products were obtained and separated using silicagel chromatography. In three cases we chose to isolate these products for spectroscopic characterizations.

*Synthesis of 3-(6’-tert-butyl-2’,6’- diphényl-6’,7’-dihydro-5’H-benzopyran-8’-yl)-2-cyanoacrylique* ***15***

1 g of aldehyde **6** (2.70 mmol) were dissolved, to a degassed solution of cyanoacetic acid (0.530 g, 6.24 mmol, 2.3 eq.) in dry acetonitrile (50 mL). 0.6 mL (6.24 mmol, 2.3 eq.) of piperidine were then added, under a nitrogen atmosphere, and the mixture was stirred at reflux temperature for 16 hours. After cooling to room temperature, acetonitrile was evaporated. Products **20** and **15** were separated after silicagel chromatography, using first CH2Cl2/AcOEt (95%/5%) as eluent to obtain **20** and CH2Cl2/AcOEt/ AcOH (75%/24%/1%) to isolate **15**. The crude products **20** and **15** were obtained by crystallization from diethylether/pentane (**15**, 730 mg, 54%, dark purple solid; **20**: 120 mg, 11%, red powder).

**Spectroscopic data**

Compound **7:** FTIR (ATR,, *cm-1*) : 3052; 2951; 2800; 2726; 645; 1576; 1449; 1288; 1143; 1078; 956; 865; 693. 1H NMR (CDCl3, ppm): 9.63 (d, 3J = 8.1 Hz, 1H) ; 8.02 (d, 3J = 15.1 Hz, 1H) ; 7.74 (m, 2H) ; 7.46 (m, 6H) ; 7.34 (m 2H) ; 6.34 (s, 1H) ; 6.12 (dd, 3J = 8.1 Hz, 3J = 15.1 Hz, 1H) ; 2.79 (d, 2J = 15.4 Hz, 1H) ; 2.57 (d, 2J = 15.4 Hz, 1H) ; 2.15 (dd, 2J = 15.4 Hz, 3J = 11.8 Hz, 1H) ; 2.07 (dd, 2J = 15.4 Hz, 3J = 13.2 Hz, 1H) ; 1.46 (t, 3J = 12.3 Hz, 1H) ; 0.91 (s, 9H). 13C NMR (CDCl3, ppm): 192.9 ; 155.7; 153.9 ; 147.3 ; 138.2 ; 137.9 ; 132.2 ; 129.9 ; 128.9 ; 128.7 ; 128.4 ; 126.1 ; 124.7 ; 122.2 ; 108.4 ; 105.3 ; 41.8 ; 32.4 ; 28.3 ; 27.2 ; 26.0.

Compound **9: :** FTIR (ATR,, *cm-1*) : 3060; 293; 2716; 1665; 1579; 1479; 1249; 1124; 1030; 949; 846; 772; 689. 1H NMR (CDCl3, ppm):  9.67 (d, 3J = 8.0 Hz, 1H) ; 7.82 (d, 3J = 14.8 Hz, 1H) ; 7.61 (m, 2H) ; 7.42 (m, 6H) ; 7.27 (m, 2H) ; 6.68 (s, 1H) ; 6.24 (dd, 3J = 14.8 Hz, 3J = 8.0 Hz, 1H) ; 2.78 (d, 2J = 15.0 Hz, 1H) ; 2.55 (d, 2J = 16.3 Hz, 1H) ; 2.10 (dd, 2J = 16.3 Hz, 3J = 11.9 Hz, 1H) ; 1.89 (dd, 2J = 15.0 Hz, 3J = 13.0 Hz, 1H) ; 1.45 (t, 3J = 12.6 Hz, 1H) ; 0.84 (s, 9H). 13C NMR (CDCl3, ppm): 192.9; 147. 9 ; 141.2 ; 140.0 ; 136.6 ; 131.8 ; 129.5 ; 128.9 ; 128.6 ; 128.2 ; 127.8 ; 126.3 ; 125.0 ; 123.7 ; 122.5 ; 41.8 ; 32.2 ; 30,7 ; 29,2 ; 27,0.

Compound **10**: m.p. 127°C. FTIR (ATR,, *cm-1*) : 3057; 2822; 2528; 2209; 1668; 1569; 1472; 1188; 897; 795; 670. 1H NMR (DMSO-*d6*, ppm):  (Major isomer: 80.7%) 12.7 (s, 1H) ; 8.30 (d, 3J=13.3 Hz, 1H) ; 8.01 (m, 4H) ; 7.56 (m, 6H) ; 7.52 (s, 1H) ; 7.49 (s, 1H) ; 5.99 (d, 3J= 13.3 Hz, 1H). (Minor isomer: 19.3%) 12.7 (s, 1H) ; 8.55 (d, 3J=13.8 Hz, 1H) ; 8.11 (m, 4H) ; 7.56 (m, 6H) ; 7.52 (s, 1H) ; 7.49 (s, 1H) ; 6.07 (d, 3J= 13.8 Hz, 1H). 13C NMR (DMSO-*d6*, ppm):  Major isomer :164.1 ; 158.3 ; 147.5 ; 146.4 ; 134.8 ; 131.7 ; 131.3 ; 129.7 ; 127.9 ; 127.4 ; 126.3 ; 117.6 ; 116.4 ; 103.6 ; 99.7. Minor isomer 165.6 ; 158.0 ; 147.5 ; 146.4 ; 135.0 ; 131.6 ; 131.3 ; 129.7 ; 127.9 ; 127.4 ; 126.3 ; 117.9 ; 116.5 ; 103.9 ; 100.3. HRMS (Q Tof 2) calcd for C21H16NO [M-CO2+H]+ 298.12319 found 298.1223 (3ppm).

Compound **11**: m.p. 198°C. FTIR (ATR,, *cm-1*) : 3056; 2933; 2457; 2198; 1647; 1557; 1462;1397; 1222; 940; 732. 1H NMR (methanol-*d*4/acetone-*d6*, ppm): 8.70 (s, 1H) ; 7.91 (m, 2H) ; 7.48 (m, 8H) ; 6.85 (s, 1H) ; 2.91 (t, 3J=6.2 Hz, 2H) ; 2.62 (t, 3J=6.2 Hz, 2H) ; 1.73 (q, 3J=6.2 Hz, 2H). 13C NMR methanol-*d*4/acetone-*d6*, ppm): 165.7 ; 160.5 ; 154.9 ; 146.1; 136.2 ; 131.0 ; 130.2 ; 128.6 ; 128.3 ; 128.1 ; 127.7 ; 124.9 ; 124.5 ; 106.9 ; 105.9 ; 26.1 ; 24.6 ; 19.9. HRMS (Q Tof 2) calcd for C25H19NO3Na [M+Na]+ 404.12626 found 404.1265 (1 ppm).

Compound **12**: m.p. 174°C. FTIR (ATR,, *cm-1*) : 2930; 2505; 2204; 1648; 562; 1375; 1113; 980; 727. 1H NMR (acetone-*d6*, ppm): 8.05 (m, 4H) ; 7.51 (m, 8H) ; 6.74 (s, 1H) ; 6.55 (dd, J3=12 Hz, J3=14 Hz, 1H) ; 2.64 (t, J3=6 Hz, 2H) ; 2.58 (t, J3=6 Hz, 2H) ; 1.78 (q , J3=6 Hz, 2H). 13C NMR (acetone-*d6*, ppm): 164.3 ; 156.6 ; 156.0 ; 154.4 ; 143.1 ; 139.4; 137.8 ; 131,8; 130.0 ; 129.0 ; 128.8 ; 128.6 ; 128.2 ; 125.7 ; 125.1 ; 117.0 ; 110.0 ; 105.6 ; 27.1 ; 24.4 ; 20.5. HRMS (Q Tof 2) calcd for C27H21NO3Na [M+Na] + 430.14191 found 430.1418 (0 ppm).

Compound **13**: m.p. 172°C. FTIR (ATR,, *cm-1*) : 2939; 2205; 1651; 1586; 1538; 1468 ; 1404; 1217; 1170; 1018; 932; 759. 1H NMR (acetone-*d6*, ppm): 8.42 (s, 1H) ; 7.77 (m, 2H) ; 7.48 (m, 8H) ; 7.06 (s, 1H) ; 2.91 (t, 3J=6.2 Hz, 2H) ; 2.62 (t, 3J = 6.2 Hz, 2H) ; 1.81 (q, 3J=6.2 Hz, 2H). 13C NMR (acetone-*d6*, ppm): 164.8 ; 149.2 ; 147.5 ; 143.2 ; 142.9 ; 140.6 ; 136.5 ; 131.3 ; 130.0 ; 129.3 ; 128.7 ; 128.3 ; 128.1 ; 126.4 ; 123.6 ; 122.0 ; 117.6 ; 28.9 ; 27.9 ; 20.3. HRMS (Q Exactive) calcd for C25H18NO2S [M-H]- 396.10583 found 396.1062 (0 ppm).

Compound **14**: m.p. 184°C. FTIR (ATR,, *cm-1*) : 2211; 1649; 1554; 1483; 1355; 1121; 966; 753. 1H NMR (DMSO-*d6*, ppm): 13.2 (s, 1H) ; 8.17 (d, J3=12.4 Hz, 1H) ; 7.87 (d, J3=14.2 Hz, 1H) ; 7.74 (m, 2H) ; 7.43 (m, 8H) ; 6.86 (s, 1H) ; 6.56 (dd, J3= 12.4 Hz, J3= 14.2 Hz, 1H) ; 2.45 (m, 4H) ; 1.65 (q, 3J = 5.90 Hz, 2H). 13C NMR (DMSO-*d6*, ppm): 164.6 ; 156.0 ; 156 ; 144.9 ; 143.0 ; 141.0 ; 140.7 ; 138.2 ; 136.1 ; 131.7 ; 130.3 ; 129.6 ; 129.0 ; 128,8 ; 128.3 ; 125.6 ; 122.7 ; 120.7 ; 116.6 ; 29.5 ; 27.1 ; 20.5. HRMS (Q Exactive) calcd for C27H20NO2S [M-H]- 422.12148 found 422.1222 (0 ppm).

Compound **15**: m.p. 192°C. FTIR (ATR,, *cm-1*) : 2955; 2203; 1627; 1552; 1467; 1206; 1039; 938; 763; 686. 1H NMR (acetone-*d*6, ppm): 8.74 (s, 1H) ; 7.97 (m, 2H) ; 7.54 (m, 8H) ; 6.90 (s, 1H) ; 3.34 (d, 2J=15.7 Hz, 1H) ; 2.86 (s, 1H) ; 2.48 (dd, 3J=12.0 Hz, 2J=15.7 Hz, 1H) ; 2.32 (dd, 3J=13.0 Hz, 2J=16.3 Hz, 1H) ; 1.48 (ft, 3J=12.1 Hz, 1H) ; 0.94 (s, 9H). 13C NMR (acetone-*d*6, ppm): 165.5 ; 160.3 ; 155.1 ; 146.3 ; 137.3 ; 131.6 ; 130.4 ; 129.0 ; 128.8 ; 128.6 ; 128.3 ; 126.0 ; 125.0 ; 118.3 ; 107.5 ; 106.4 ; 41.9 ; 32.0 ; 27.9 ; 26.6 ; 26.5. HRMS (Q Tof 2) calcd for C29H27NO3Na [M+Na] + 460.18886 found 460.1887 (0 ppm).

Compound **16**: m.p. 194°C. FTIR (ATR,, *cm-1*) : 2955; 2210; 1655; 1442; 1130; 978; 758. 1H NMR (acetone-*d6*, ppm): 8.10 (m, 1H) ; 8.07 (m, 1H) ; 8.04 (m, 2H) ; 7.52 (m, 8H) ; 6.74 (s, 1H) ; 6.59 (dd, 3J=11.7 Hz, 3J=14.4 Hz, 1H) ; 2.87 (d, 2J= 15.8 Hz, 1H) ; 2.74 (d, 2J= 15.8 Hz, 1H) ; 2,29 (m, 2H) ; 1.50 (t, 3J= 12.3 Hz, 1H) ; 0.95 (s, 9H). NMR (DMSO-*d6*, ppm):  13.0 (s, 1H) ; 8.19 (d, 3J= 12.3 Hz, 1H) ; 8.04 (m, 2H) ; 7.95 (d, 3J= 14.4 Hz, 1H) ; 7.50 (m, 8H) ; 6.83 (s, 1H) ; 6.41 (dd, 3J=12.3 Hz, 3J= 14.4 Hz, 1H) ; 2.68 (d, 3J=16.3 Hz, 1H) ; 2.58 (s, 1H) ; 2.20 (m, 2H) ; 1.38 (t, 2J=11.2 Hz, 1H); 0.87 (s, 9H). 13C NMR (DMSO-*d6*, ppm): 165.4 ; 157.0 ; 156.6 ; 154.2 ; 144.2 ; 139.7 ; 137.5 ; 131.7 ; 130.6 ; 129.5 ; 129.1 ; 129.0 ; 128.9 ; 126.6 ; 125.6 ; 117.3 ; 117.2 ; 110.2 ; 106.3 ; 41.6 ; 32.3 ; 28.2 ; 27.4 ; 25.8. HRMS (Q Tof 2) calcd for C30H30NO [M-CO2+H]+ 420.23274 found 420.2323 (1 ppm).

Compound **17**: m.p. 178°C. FTIR (ATR,, *cm-1*) : 2950; 2207; 1648; 1536; 1458; 1396; 920; 760; 679. 1H NMR (acetone-*d*6, ppm): 8.44 (s, 1H) ; 7.75 (m, 2H) ; 7.49 (m, 8H) ; 7.05 (s, 1H); 3.20 (d, 2J= 16.1 Hz, 1H) ; 2.88 (d, 2J= 15.4 Hz, 1H) ; 2.51 (dd, 3J= 12.4 Hz, 2J= 16.1 Hz, 1H) ; 2.12 (m, 1H) ; 1.50 (t, 3J=12.5 Hz, 1H) ; 0.89 (s, 9H). 13C NMR (acetone-*d*6, ppm): 165.1 ; 149.3 ; 147.5 ; 142.9 ; 139.7 ; 136.0 ; 132.4 ; 130.0 ; 129.2 ; 128.7 ; 128.3 ; 128.2 ; 126.4 ; 123.5 ; 122.5 ; 117.5 ; 41.9 ; 32.1 ; 30.4 ; 30.3 ; 26.3. HRMS (Q exactive) calcd for C29H26NO2S [M-H]- 452.16843 found 452.1690 (0 ppm).

Compound **18**: m.p.165°C. FTIR (ATR,, *cm-1*) : 2959; 2219; 1675; 1558; 1457; 1283; 1123; 757; 689. 1H NMR (acetone-*d6*, ppm): 8.14 (d, 3J= 12.1 Hz, 1H) ; 7.88 (d, 3J= 14.0 Hz, 1H) ; 7.75 (m, 2H) ; 7.49 (m, 6H) ; 7.41 (m, 2H) ; 6.86 (s, 1H) ; 6.77 (dd, 3J= 12.1 Hz, 3J= 14.0 Hz, 1H) ; 2.84 (d, 2J= 15.4 Hz, 1H) ; 2.72 (d, 2J= 16.8 Hz, 1H) ; 2.25 (dd, 3J= 12.0 Hz, 2J= 15.4 Hz, 1H) ; 2.03 (s, 1H) ; 149 (t, 3J= 11.3 Hz, 1H) ; 0.89 (s, 9H). 13C NMR (acetone-*d6*, ppm): 163.4 ; 155.7 ; 144.4 ; 142.7 ; 141.2 ; 140.5 ; 138.1; 136.3 ; 132.4 ; 129.6 ; 129.0 ; 128.7 ; 128.3 ; 127.9 ; 126.2 ; 125.0 ; 122.5 ; 120.3 ; 115.4 ; 41.8 ; 31.9 ; 30.6 ; 28.7 ; 26.5. HRMS (Q Tof 2) calcd for C31H28NO2S [M-H]- 478.18408 found 478.1846 (0 ppm).

Compound **19**: FTIR (ATR,, *cm-1*) : 3057; 2930; 2199; 1635; 1575; 1493; 1368; 1295; 1195; 1128; 953; 841; 687. 1H NMR (CDCl3, ppm): 7.91 (d, 3J=16.0 Hz, 1H) ; 7.72 (m, 2H) ; 7.46 (m, 5H) ; 7.33 (m, 2H)  ; 6.27 (s, 1H) ; 5.04 (d, 3J=16.0 Hz, 1H) ; 2.53 (t, 3J=6.1 Hz, 2H) ; 2.34 (t, 3J=6.1 Hz, 2H) ; 1.72 (q, 3J=6.1 Hz, 1H). 13C NMR (CDCl3, ppm): 153.7 ; 153.3 ; 143.3 ; 138.1 ; 136.9 ; 132.4 ; 129.7 ; 128.9 ; 128.5 ; 128.3 ; 128.2 ; 124.7 ; 120.4 ; 106.2 ; 104.5 ; 85.5 ; 27.0 ; 23.6 ; 20.3 (C7). HRMS (Q Tof 2) calcd for C24 H19NONa [M+Na]+  360.13643 found 360.1367 (1 ppm).

Compound **20**: FTIR (ATR,, *cm-1*) : 3051; 2951; 2193; 1636; 1572; 1493; 1247; 1156; 951; 762; 701; 690. 1H NMR (CDCl3, ppm):  7.91 (d, 3J=16.0 Hz, 1H) ; 7.72 (m, 2H) ; 7.46 (m, 5H) ; 7.33 (m, 2H) ; 6.27 (s, 1H) ; 5.03 (d, 3J=16.0 Hz, 1H) ; 2.76 (d, 2J=15.2 Hz, 1H) ; 2.39 (d, 2J=15.4 Hz, 1H); 2.03 (m, 2H) ; 1.43 (t, 3J=12.3 Hz, 1H) ; 0.89 (s, 9H). 13C NMR (CDCl3, ppm): 153.7 ; 153.3 ; 144.3 ; 138.1 ; 137.0 ; 132.1 ; 129.7 ; 128.9 ; 128.6 ; 128.2 ; 128.0 ; 125.0 ; 121.5 ; 106.9 ; 104.6 ; 86.4 ; 41.6 ; 32.2 ; 28.0 ; 27.2 ; 25.2. HRMS (Q Tof 2) calcd for C28 H27 N O Na [M+Na] + 416.19903 found 416.1992 (0 ppm).

Compound **21**: m.p. 157°C. FTIR FTIR (ATR,, *cm-1*) : 3051; 2950; 2193; 1636; 1492; 1368; 1076; 951; 825; 691. 1H NMR (CDCl3, ppm):  7.73 (d, 3J=15.7 Hz, 1H) ; 7.58 (m, 2H) ; 7.42 (m, 5H) ; 7.26 (m, 2H) ; 6.64 (s, 1H) ; 5.23 (d, 3J=15.7 Hz, 1H) ; 2.75 (d, 2J=14.2 Hz, 1H) ; 2.38 (d, 2J=16.4 Hz, 1H) ; 2.01 (dd, 3J=12.5 Hz, 2J=16.4 Hz, 1H) ; 1.85 (t, 3J=14.2 Hz, 1H) ; 1.43 (t, 3J=11.4 Hz, 1H) ; 0.84 (s, 9H). 13C NMR (CDCl3, ppm): 145.6 ; 141.2 ; 139.8 ; 139.3 ; 136.8 ; 136.5 ; 130.9 ; 129.4 ; 128.9 ; 128.6 ; 127.6 ; 126.2 ; 122.5 ; 122.1 ; 120.5 ; 90.5 ; 41.7 (C7) ; 32.2 ; 30.5 ; 28.3; 26.9. HRMS (Q Tof 2) calcd for C28H27NSNa [M+Na] + 432.17619 found 432.176 (0 ppm).

UV-vis spectra of dyes **10**-**18:**  (103.M-1.cm-1) *vs*  (nm)

**Figure S1**. UV-Vis absorption spectrum of dyes **10** in solutiondans CH2Cl2 (C= 5.10-5 mol.L-1)

**Figure S2**. UV-Vis absorption spectra of dyes **11-14** in solutiondans CH2Cl2 (C= 5.10-5 mol.L-1)

**Figure S3**. UV-Vis absorption spectra of dyes **15-18** in solutiondans CH2Cl2 (C= 5.10-5 mol.L-1)

**Cell preparation and photovoltaic measurements**

FTO conductive glass substrates (F-doped SnO2) were purchased from Pilkington (TEC8). The plates were cleaned by successive sonication in soapy water, then an ethanolic solution of HCl (0.1 M) for 10 minutes, and finally dried in air. TiO2 films were prepared in three steps. A first treatment is applied by immersion for 30 min in an aqueous TiCl4 solution at 80°C. Three successive layers of mesoporous TiO2 were then screen printed using a transparent colloidal paste (Dyesol DSL 18NR-T) and a final light scattering layer (Dyesol DSL 18NR-AO) was affixed, with 20-minute long drying steps at 150°C between each layer. Overall, the thickness of the mesoporous layer is 12 µm, and the thickness of the scattering layer is 4 µm. The obtained substrates were then sintered at 450°C, following a progressive heating ramp (325°C for 5 min, 375°C for 5 min, 450°C for 30 min). A second TiCl4 treatment was immediately conducted afterwards and the electrodes were fired one last time at 450°C for 30 minutes. Thicknesses (16 µm) were measured by a Sloan Dektak 3 profilometer. The prepared TiO2 electrodes were soaked while still hot (ca. 80°C) in a 0.25 mM solution of complexes **11**-**18** in a mixture of dichloromethane and ethanol (3/2 v/v). After one night of dyeing, the electrodes were rinsed in ethanol and dried in air, in the dark. Platinum based counter electrodes were prepared by drop casting two drops of hexachloroplatinic acid in distilled isopropanol (2 mg per mL) on FTO plates, and subsequent firing at 380°C for 30 minutes. The photoelectrode and the counter electrode were placed on top of each other and sealed using a thin transparent film of Surlyn polymer (DuPont, 60 µm) as a spacer. The resulting chamber was filled with an iodine-based electrolyte (30 mM I2, 0.1 M LiI, 0.1 M guanidinium thiocyanate, 0.6 M 1-ethyl-2,3-dimethylimidazolium iodide and 0.1 M 4-tertbutylpyridine when mentioned, in dry distilled acetonitrile) by vacuum back filling through a predrilled hole in the counter electrode, and the photovoltaic device was sealed afterwards with Surlyn and a cover glass. The cell had an active area of 0.25 cm2. Photovoltaic measurements were performed with a calibrated AM 1.5 artificial solar light simulator (Oriel) and a Keithley 2400 digital source-meter; data were collected with a local software designed by Synervia (labview).

**Figure S4**. Normalized UV-Vis absorption spectra of dyes **11** (grey), **12** (yellow), **15** (blue) and **16** (red) chemisorbed on 4 µm thick transparent TiO2 films.

**Figure S5** . Normalized UV-Vis absorption spectra of dyes **13** (red), **14** (black), **17** (blue) and **18** (green) chemisorbed on 4 µm thick transparent TiO2 films.

**Figure S6**. J-V curves recorded in the dark for DSSC based on dyes **11** (solid line, upper) and **15** (dotted line, upper), dyes **12** (solid line, lower) and **16** (dotted line, lower).

**Figure S7**. IPCE spectra of DSSC where TiO2 was sensitized by dyes **13** (grey line), **14** (yellow line), **17** (blue line) and **18** (red line).

**Figure S8**. J-V curve recorded in the dark for dyes differing only by the nature of X (X = O: red line; X = S, black line). A: dyes **11** and **13**. B: dyes **12** and **14**. C: dyes **15** and **17**. D: dyes **16** and **18**.

**Table S1**. Performances of TiO2 based DSSC associated to dye **11** recorded under simulated sunlight AM1.5, when 0, 5 and 20 mM CDCA were added to the dyeing bath.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Jsc  (mA/cm²) | Voc  (mV) | FF  (%) | Η  (%) | [CDCA]  mM |
| 4.22 ± 0.12 | 576 ± 2 | 77.4 ± 0.1 | 1.88 ± 0.04 | 0 mM CDCA |
| 2.91 ± 0.12 | 587 ± 2 | 78.1 ± 0.1 | 1.33 ± 0.06 | 5 mM CDCA |
| 1.39 ± 0.11 | 573 ± 3 | 78.1 ± 0.1 | 0.62 ± 0.04 | 20 mM CDCA |

**Figure S9**. J-V curves for DSSC where the dyeing bath contains 0.25 mM **11** and 0 (solid line), 5 mM (dashed line) and 20 mM chenodeoxycholic acid (dash-dot line) under AM 1.5 irradiation.

1. \* Françoise Robin – Le Guen. Tel.: +33 296469446; fax: : +33 296469354; francoise.le-guen@univ-rennes1.fr [↑](#footnote-ref-1)