

Supporting Information

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

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CONTENTS	Page N°
General experimental informations	2
Synthetic procedures 7-9, 10-18	3
Spectroscopic Data 10-21	4
UV-Vis spectra of dyes 10-18 :	7
Figure S1. UV-Vis absorption spectrum of dyes 10	7
Figure S2. UV-Vis absorption spectra of dyes 11-14	7
Figure S3. UV-Vis absorption spectra of dye 15-18	7
Cell preparation and photovoltaic measurements	8
Figure S4. Normalized UV-Vis absorption spectra of dyes 11, 12, 15 and 16 chemisorbed on 4 μm thick transparent TiO_2 films	9
Figure S5. Normalized UV-Vis absorption spectra of dyes 13, 14, 17 and 18 chemisorbed on 4 μm thick transparent TiO_2 films	9
Figure S6. J-V curves recorded in the dark for DSSC based on dyes 11, 15, 12 and 16	10
Figure S7. IPCE spectra of DSSC where TiO_2 was sensitized by dyes 13, 14, 17 and 18	11
Figure S8. J-V curve recorded in the dark for dyes differing only by the nature of X (X = O: X = S. for dyes 11 and 13, 12 and 14, 15 and 17, dyes 16 and 18.	12
Table S1. Performances of TiO_2 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.	14
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.

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 ^{13}C NMR Spectra were recorded at room temperature in CDCl_3 , $\text{DMSO}-d_6$ or acetone- d_6 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 CH_2Cl_2 - $[\text{Bu}_4\text{N}][\text{PF}_6]$. 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 $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$ was measured experimentally with reference to the standard calomel electrode (SCE): $E_{1/2}(\text{Fc}^+/\text{Fc}) = 0.41 \text{ V vs. SCE}$, and recalibrated vs. NHE assuming that $E^0(\text{SCE}) = 0.24 \text{ V vs. NHE}$.

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 synthesized 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, $\bar{\nu}$, cm^{-1}): 3052; 2951; 2800; 2726; 645; 1576; 1449; 1288; 1143; 1078; 956; 865; 693. ^1H NMR (CDCl_3 , ppm): δ 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). ^{13}C NMR (CDCl_3 , ppm): δ 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, $\bar{\nu}$, cm^{-1}): 3060; 293; 2716; 1665; 1579; 1479; 1249; 1124; 1030; 949; 846; 772; 689. ^1H NMR (CDCl_3 , ppm): δ 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). ^{13}C NMR (CDCl_3 , ppm): δ 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, $\bar{\nu}$, cm^{-1}): 3057; 2822; 2528; 2209; 1668; 1569; 1472; 1188; 897; 795; 670. ^1H NMR ($\text{DMSO}-d_6$, ppm): δ (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). ^{13}C NMR ($\text{DMSO}-d_6$, ppm): δ 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 $\text{C}_{21}\text{H}_{16}\text{NO}$ [$\text{M}-\text{CO}_2+\text{H}$] $^+$ 298.12319 found 298.1223 (3ppm).

Compound **11**: m.p. 198°C. FTIR (ATR, $\bar{\nu}$, cm^{-1}): 3056; 2933; 2457; 2198; 1647; 1557; 1462; 1397; 1222; 940; 732. ^1H NMR (methanol- d_4 /acetone- d_6 , ppm): δ 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). ^{13}C NMR (methanol- d_4 /acetone- d_6 , ppm): δ 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 $\text{C}_{25}\text{H}_{19}\text{NO}_3\text{Na}$ [$\text{M}+\text{Na}$] $^+$ 404.12626 found 404.1265 (1 ppm).

Compound **12**: m.p. 174°C. FTIR (ATR, $\bar{\nu}$, cm^{-1}): 2930; 2505; 2204; 1648; 562; 1375; 1113; 980; 727. ^1H NMR (acetone- d_6 , ppm): δ 8.05 (m, 4H); 7.51 (m, 8H); 6.74 (s, 1H); 6.55 (dd, $J^3 = 12$ Hz, $J^3 = 14$ Hz, 1H); 2.64 (t, $J^3 = 6$ Hz, 2H); 2.58 (t, $J^3 = 6$ Hz, 2H); 1.78 (q, $J^3 = 6$ Hz, 2H). ^{13}C NMR (acetone- d_6 , ppm): δ 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 $\text{C}_{27}\text{H}_{21}\text{NO}_3\text{Na}$ [$\text{M}+\text{Na}$] $^+$ 430.14191 found 430.1418 (0 ppm).

Compound **13**: m.p. 172°C. FTIR (ATR, $\bar{\nu}$, cm^{-1}): 2939; 2205; 1651; 1586; 1538; 1468; 1404; 1217; 1170; 1018; 932; 759. ^1H NMR (acetone- d_6 , ppm): δ 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). ^{13}C NMR (acetone- d_6 , ppm): δ 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 $C_{25}H_{18}NO_2S [M-H]^-$ 396.10583 found 396.1062 (0 ppm).

Compound **14**: m.p. 184°C. FTIR (ATR, $\bar{\nu}$, cm^{-1}): 2211; 1649; 1554; 1483; 1355; 1121; 966; 753. 1H NMR (DMSO- d_6 , ppm): δ 13.2 (s, 1H) ; 8.17 (d, $J^3=12.4$ Hz, 1H) ; 7.87 (d, $J^3=14.2$ Hz, 1H) ; 7.74 (m, 2H) ; 7.43 (m, 8H) ; 6.86 (s, 1H) ; 6.56 (dd, $J^3=12.4$ Hz, $J^3=14.2$ Hz, 1H) ; 2.45 (m, 4H) ; 1.65 (q, $^3J=5.90$ Hz, 2H). ^{13}C NMR (DMSO- d_6 , ppm): δ 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 $C_{27}H_{20}NO_2S [M-H]^-$ 422.12148 found 422.1222 (0 ppm).

Compound **15**: m.p. 192°C. FTIR (ATR, $\bar{\nu}$, cm^{-1}): 2955; 2203; 1627; 1552; 1467; 1206; 1039; 938; 763; 686. 1H NMR (acetone- d_6 , ppm): δ 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). ^{13}C NMR (acetone- d_6 , ppm): δ 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 $C_{29}H_{27}NO_3Na [M+Na]^+$ 460.18886 found 460.1887 (0 ppm).

Compound **16**: m.p. 194°C. FTIR (ATR, $\bar{\nu}$, cm^{-1}): 2955; 2210; 1655; 1442; 1130; 978; 758. 1H NMR (acetone- d_6 , ppm): δ 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- d_6 , ppm): δ 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). ^{13}C NMR (DMSO- d_6 , ppm): δ 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 $C_{30}H_{30}NO [M-CO_2+H]^+$ 420.23274 found 420.2323 (1 ppm).

Compound **17**: m.p. 178°C. FTIR (ATR, $\bar{\nu}$, cm^{-1}): 2950; 2207; 1648; 1536; 1458; 1396; 920; 760; 679. 1H NMR (acetone- d_6 , ppm): δ 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). ^{13}C NMR (acetone- d_6 , ppm): δ 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 $C_{29}H_{26}NO_2S [M-H]^-$ 452.16843 found 452.1690 (0 ppm).

Compound **18**: m.p.165°C. FTIR (ATR, $\bar{\nu}$, cm^{-1}): 2959; 2219; 1675; 1558; 1457; 1283; 1123; 757; 689. 1H NMR (acetone- d_6 , ppm): δ 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) ; 1.49 (t, $^3J=11.3$ Hz, 1H) ; 0.89 (s, 9H). ^{13}C NMR (acetone- d_6 , ppm): δ 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 $C_{31}H_{28}NO_2S [M-H]^-$ 478.18408 found 478.1846 (0 ppm).

Compound **19**: FTIR (ATR, $\bar{\nu}$, cm^{-1}): 3057; 2930; 2199; 1635; 1575; 1493; 1368; 1295; 1195; 1128; 953; 841; 687. 1H NMR ($CDCl_3$, ppm): δ 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). ^{13}C NMR ($CDCl_3$, ppm): δ 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 (C_7). HRMS (Q ToF 2) calcd for $C_{24}H_{19}NONa [M+Na]^+$ 360.13643 found 360.1367 (1 ppm).

Compound **20**: FTIR (ATR, $\bar{\nu}$, cm^{-1}): 3051; 2951; 2193; 1636; 1572; 1493; 1247; 1156; 951; 762; 701; 690. 1H NMR ($CDCl_3$, ppm): δ 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). ^{13}C NMR ($CDCl_3$, ppm): δ 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 $C_{28}H_{27}NO Na [M+Na]^+$ 416.19903 found 416.1992 (0 ppm).

Compound **21**: m.p. 157°C. FTIR FTIR (ATR, $\bar{\nu}$, cm^{-1}): 3051; 2950; 2193; 1636; 1492; 1368; 1076; 951; 825; 691. 1H NMR ($CDCl_3$, ppm): δ 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). ^{13}C NMR ($CDCl_3$, ppm): δ 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 (C_7) ; 32.2 ; 30.5 ; 28.3 ; 26.9. HRMS (Q ToF 2) calcd for $C_{28}H_{27}NSNa [M+Na]^+$ 432.17619 found 432.176 (0 ppm).

UV-vis spectra of dyes **10-18**: ϵ ($10^3 \cdot M^{-1} \cdot cm^{-1}$) vs λ (nm)

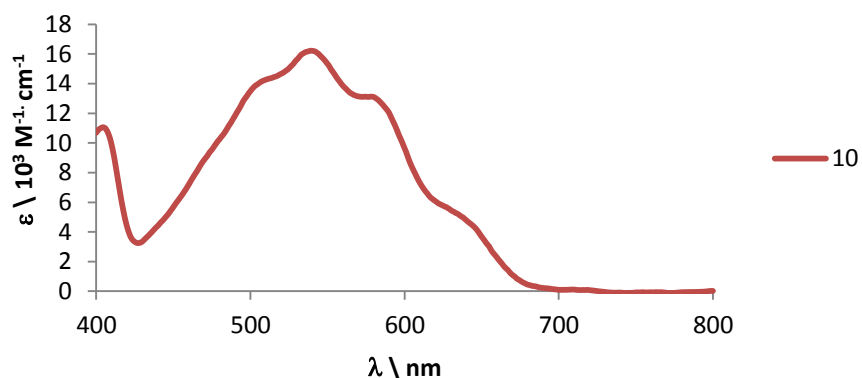


Figure S1. UV-Vis absorption spectrum of dyes **10** in solution dans CH_2Cl_2 ($C= 5 \cdot 10^{-5} \text{ mol.L}^{-1}$)¹⁾

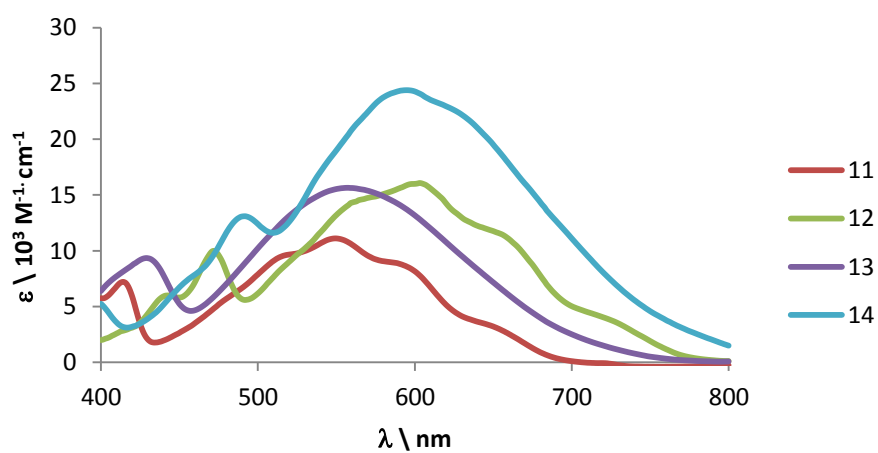


Figure S2. UV-Vis absorption spectra of dyes **11-14** in solution dans CH_2Cl_2 ($C= 5 \cdot 10^{-5} \text{ mol.L}^{-1}$)

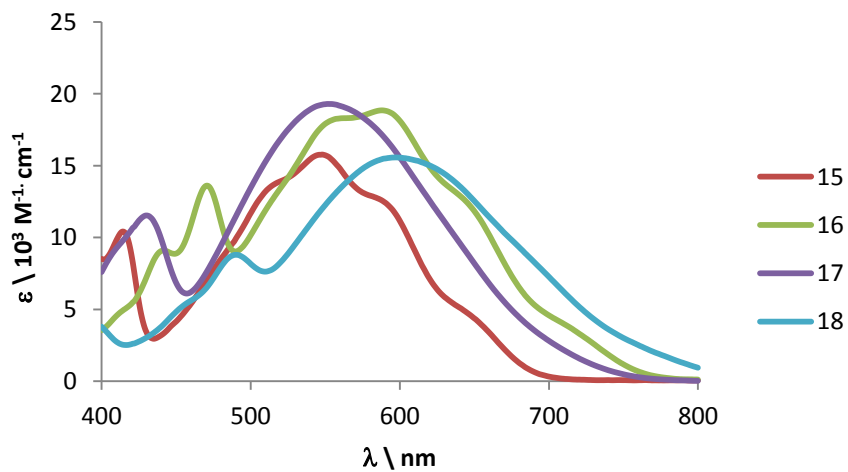


Figure S3. UV-Vis absorption spectra of dyes **15-18** in solution dans CH_2Cl_2 ($C= 5.10^{-5}$ mol.L⁻¹)

Cell preparation and photovoltaic measurements

FTO conductive glass substrates (F-doped SnO_2) 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. TiO_2 films were prepared in three steps. A first treatment is applied by immersion for 30 min in an aqueous TiCl_4 solution at 80°C. Three successive layers of mesoporous TiO_2 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 TiCl_4 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 TiO_2 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 I_2 , 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).

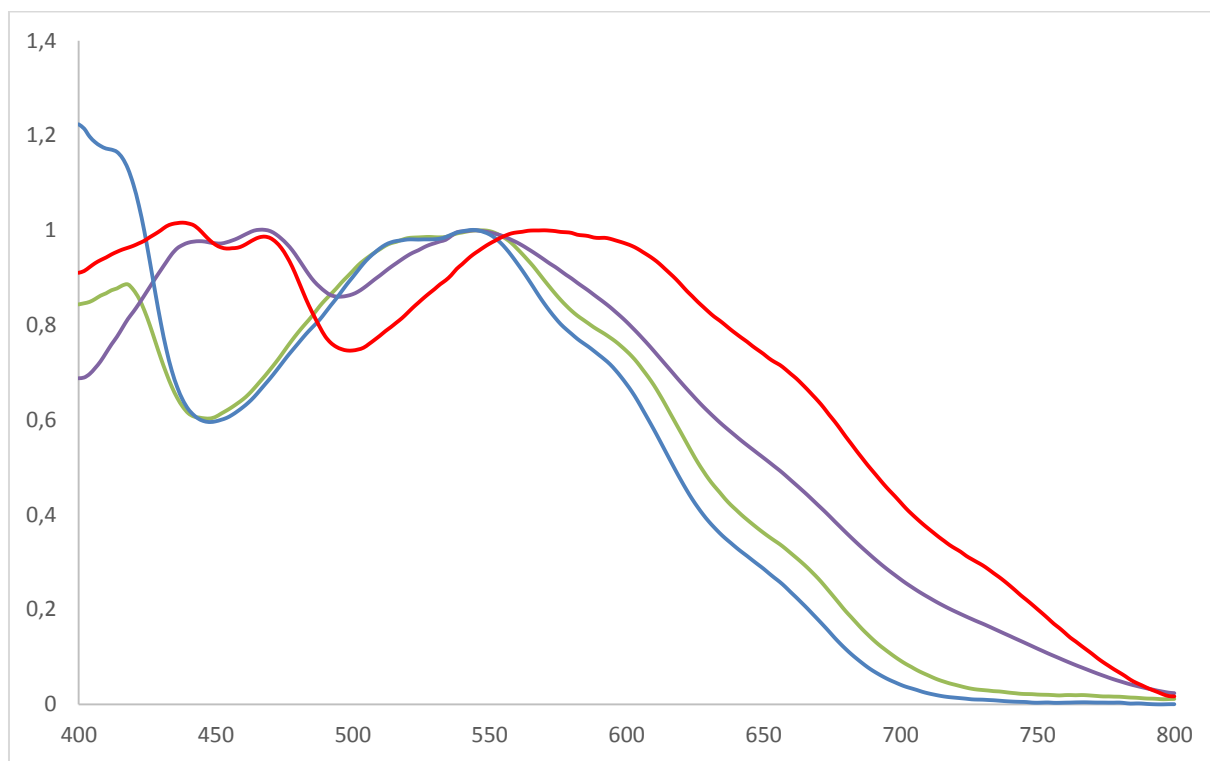


Figure S4. Normalized UV-Vis absorption spectra of dyes **11** (grey), **12** (yellow), **15** (blue) and **16** (red) chemisorbed on 4 μm thick transparent TiO₂ films.

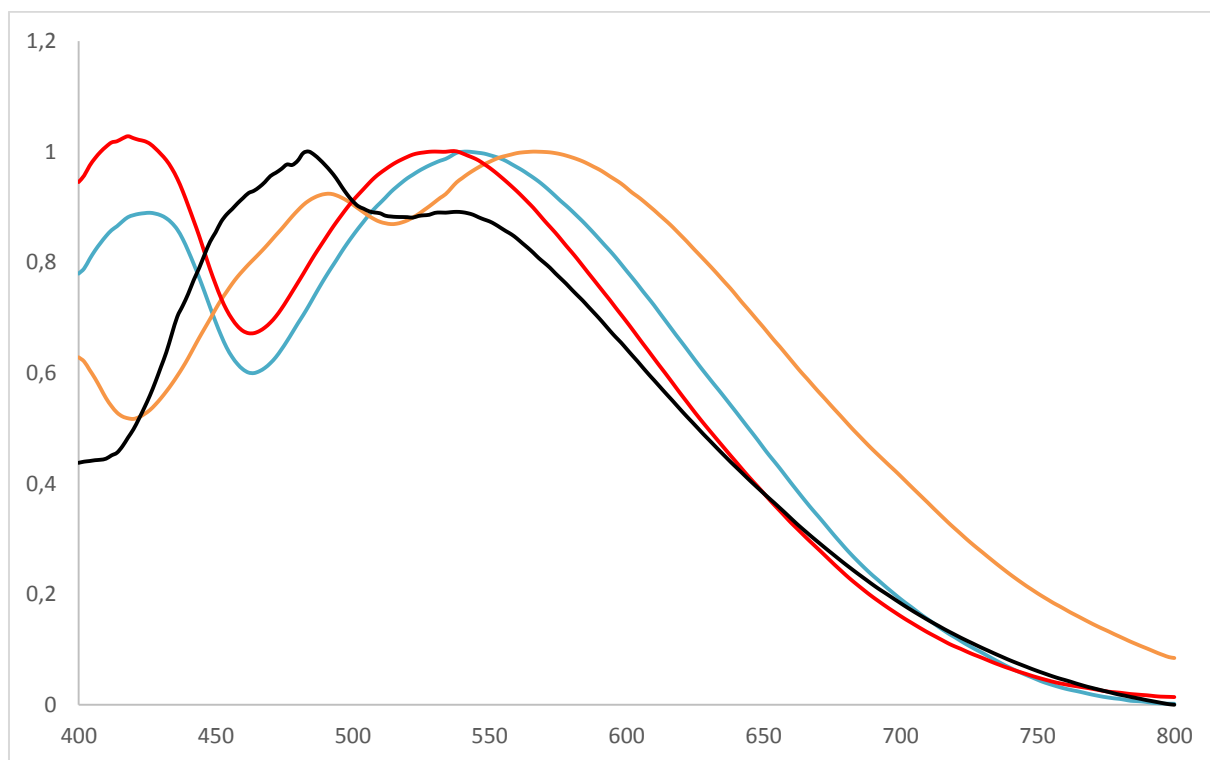


Figure S5 . Normalized UV-Vis absorption spectra of dyes **13** (red), **14** (black), **17** (blue) and **18** (green) chemisorbed on 4 μm thick transparent TiO_2 films.

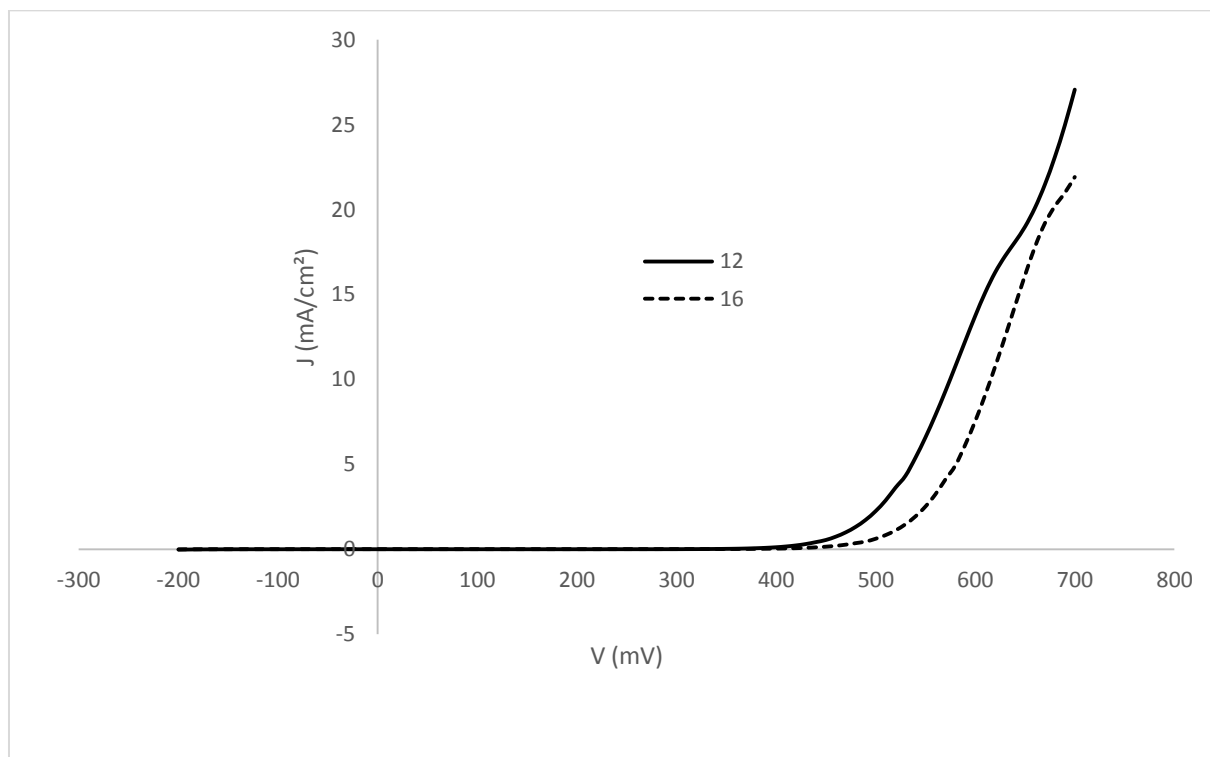
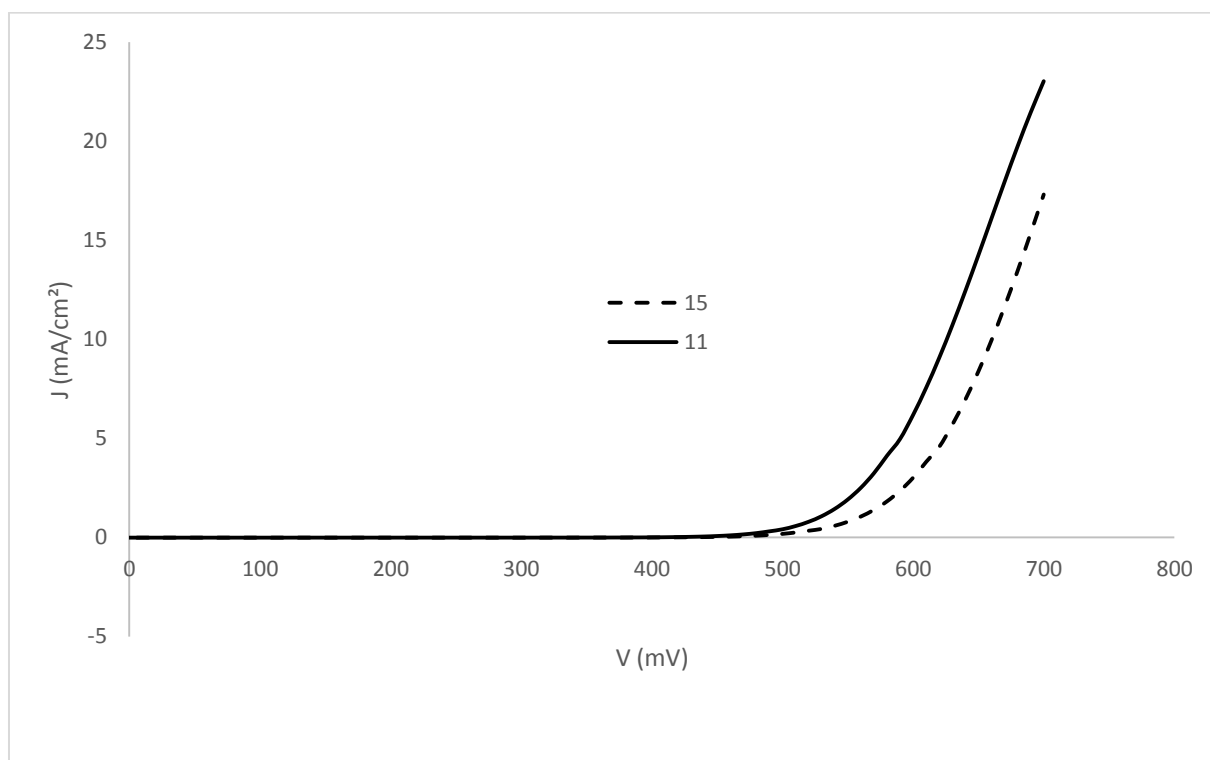


Figure S6. J-V curves recorded in the dark for DSSC based on dyes **11** (solid line, upper) and **15** (dotted line, upper), dyes **12** (solid line, lower) and **16** (dotted line, lower).

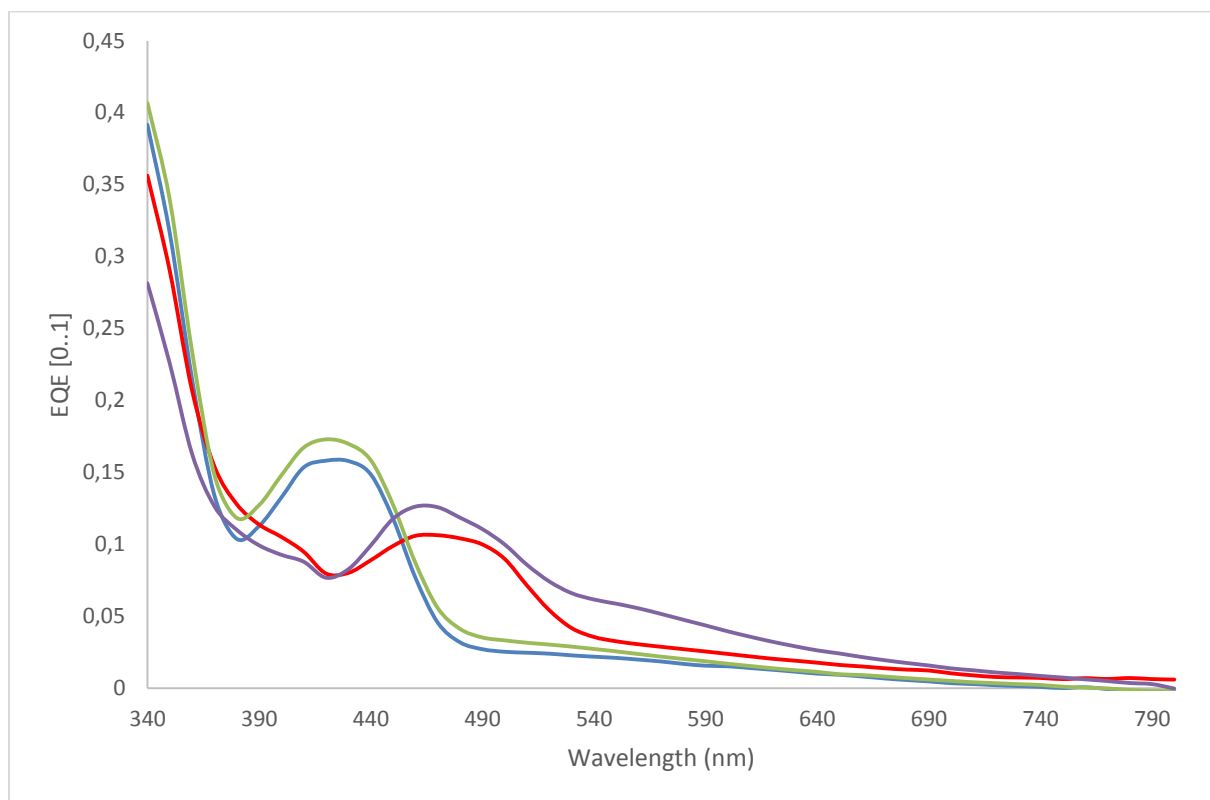


Figure S7. IPCE spectra of DSSC where TiO₂ was sensitized by dyes **13** (grey line), **14** (yellow line), **17** (blue line) and **18** (red line).

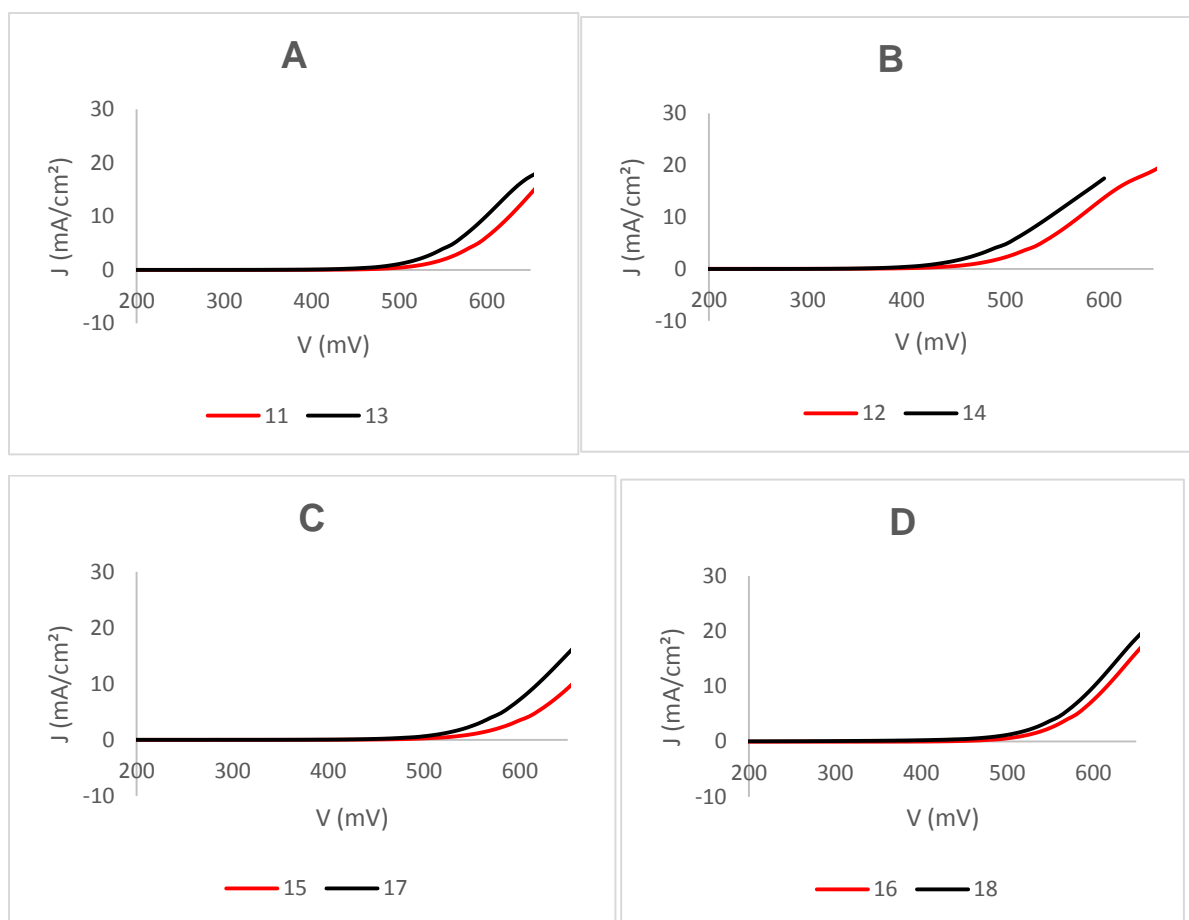


Figure S8. J-V curve recorded in the dark for dyes differing only by the nature of X (X = O: red line; X = S, black line). A: dyes **11** and **13**. B: dyes **12** and **14**. C: dyes **15** and **17**. D: dyes **16** and **18**.

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.

J _{sc} (mA/cm ²)	V _{oc} (mV)	FF (%)	H (%)	[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

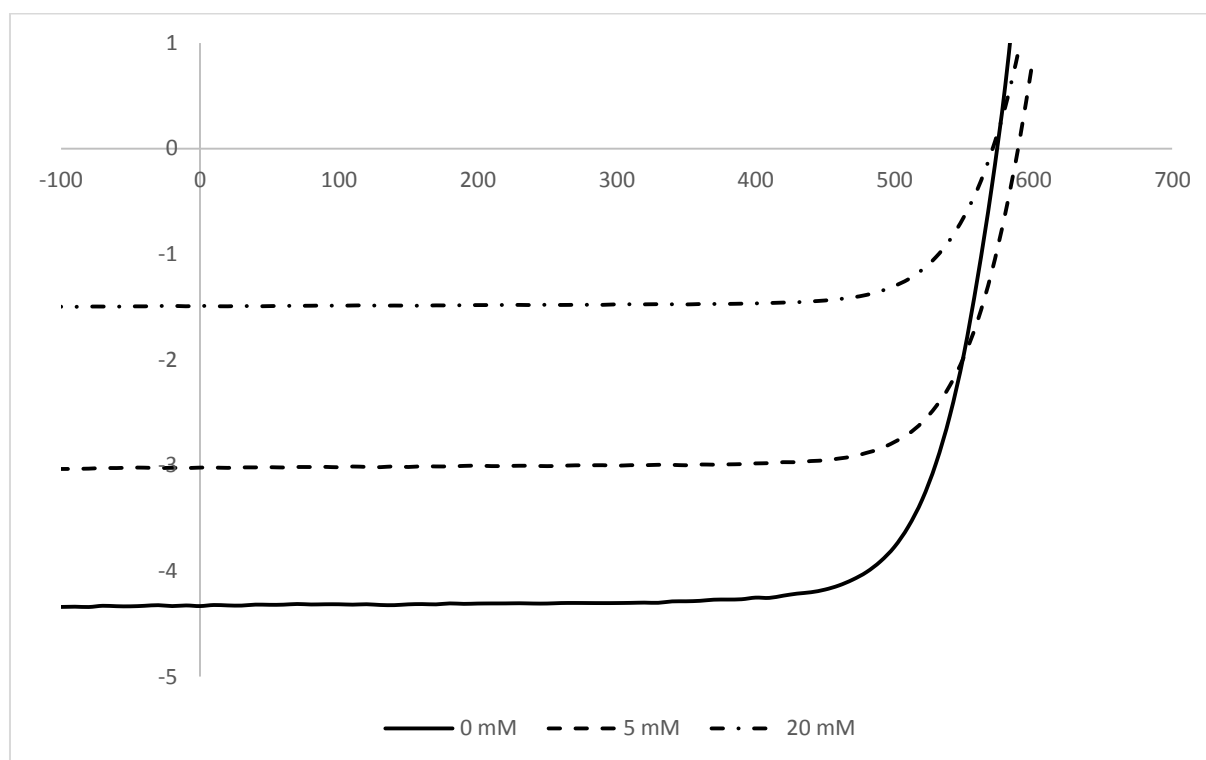


Figure S9. J-V curves for DSSC where the dyeing bath contains 0.25 mM **11** and 0 (solid line), 5 mM (dashed line) and 20 mM chenodeoxycholic acid (dash-dot line) under AM 1.5 irradiation.