Electronic Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Supramolecular light harvesting antenna to enhance absorption cross section in dye-sensitized solar cells

Julien Warnan, Yann Pellegrin, Errol Blart, Fabrice Odobel*

Laboratoire CEISAM, Equipe d'ingénierie et de photonique moléculaires
UMR CNRS 6230 - Bât. 4 Faculté des Sciences et des Techniques de Nantes
BP 92208 2, rue de la Houssinière 44322 Nantes cedex 03 France

Fabrice.odobel@univ-nantes.fr

Experimental Section

General

^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 300 MHz. Chemical shifts for ^{1}H NMR spectra are referenced relative to residual protium in the deuterated solvent ($CHCl_3$ δ = 7.26 ppm for ^{1}H and δ = 77.16 ppm for ^{13}C). Spectra were recorded at room temperature, chemical shifts are written in ppm and coupling constants in Hz. MALDI-TOF analyses were performed on a Bruker Ultraflex III, microTOF Q spectrometer in positive linear mode at 20 kV acceleration voltage with 2,5-dihydroxybenzoic acid (DHB) or dithranol as matrix.UV-Visible absorption spectra were recorded on a UV-2401PC Shimadzu spectrophotometer. Fluorescence spectra were recorded on a SPEX Fluoromax fluorimeter.

Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with Merck 5735 Kieselgel $60F_{254}$. Column chromatography was carried out either with Merck 5735 Kieselgel 60F (0.040-0.063 mm mesh). Chemicals were purchased from Sigma-Aldrich and used as received. Titanium dioxide screen printing pastes were purchased from Solaronix SA (Switzerland) and Dyesol SA. Syringe filters were purchased from VWR. Compounds **D**[1], **1**[2] and **2**[3] were prepared according to literature methods.

Preparation of Dye-Sensitized Nanocrystalline TiO_2 Electrodes:

Conductive glass substrates (F-doped SnO_2) were purchased from Pilkington (TEC8, sheet resistance 8 Ω/square). Conductive glass substrates were successively cleaned by sonication in soapy water, then ethanol for 10 min before being fired at 450 °C for 30 min. Once cooled down to room temperature, FTO plates were rinsed with ethanol and dried in ambient air. TiO_2 films were then prepared in three steps. A first treatment is applied by immersion for 30 min in an aqueous $TiCl_4$ solution at 80°C. Layers of TiO_2 were then screen printed with transparent colloidal paste Ti-Nanoxide T20/SP and light scattering Ti-Nanoxide 300 as final layer, with drying steps at 150°C for 20 min between each layer. 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 applied while cells are still hot. Thicknesses were measured by a Sloan Dektak 3 profilometer. The prepared TiO_2 electrodes were soaked while still hot (80°C) in a 0.2 mM solution of **D** with 5 mmol of deoxycholic acid in a mixture of ethanol/tetrahydrofurane (1/1, v/v), during 16 h.
Cells, assembled with **A1** or **A2**, were immersed in an antenna solution at 0.2 mmol in distilled solvent for the appropriate time before being removed and quickly rinsed with ethanol.

Dye-Sensitized Solar Cell fabrication:

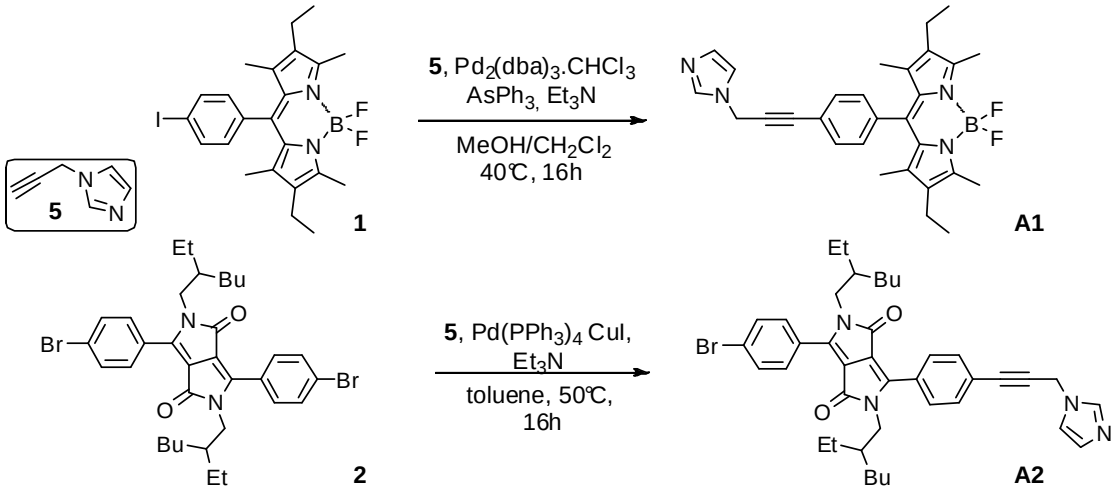
Solar cell devices were prepared using the dye-sensitized electrodes as the working electrodes and platinum-coated conducting glass electrodes as counter electrodes. The antenna free electrolyte used in both cases is composed of 0.6 M 1,2-dimethyl-3-butylimidazolium iodide, 0.1 M LiI and 0.05 M I_2 in acetonitrile. Antenna containing electrolytes were prepared by adding the suitable amount of antenna in the above electrolyte, followed by a filtration through a syringe filter (0.2 µm PTFE). Counter electrodes were prepared by chemical deposition of platinum from hexachloroplatinic acid in distilled isopropanol (2 mg per mL). The two electrodes were placed on top of each other using a thin transparent film of Surlyn polymer (DuPont, 25 µm) as a spacer to form the electrolyte space. The empty cell was tightly held, and the edges were heated to 110°C to seal the two electrodes together. A drop of electrolyte was introduced 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 *ca.* 0.25 cm^2.

Photoelectrochemical Measurements:

The current-voltage characteristics were determined by applying an external potential bias to the cell and measuring the photocurrent using a Keithley model 2400 digital source meter. The overall conversion efficiency (η) of the photovoltaic cell is calculated from the integral photocurrent density (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor of the cell (FF), and the intensity of the incident light (I_{Ph}). The photovoltaic cell was illuminated with an Oriel lamp calibrated to AM 1.5 (air mass) intensity (1000 $W.m^{-2}$).

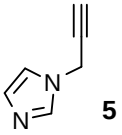
Synthesis of the antennas:



Scheme S1. Synthetic route to **A1** and **A2**

Compound 5

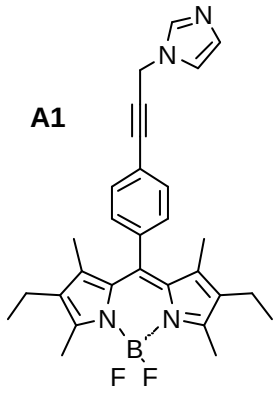
In a round-bottom flask NaH (12 mmol) and anhydrous THF (15 mL) were stirred. Then a solution of imidazole (11 mmol) in THF (20 mL) was slowly added under an argon flow. After 15 min, a solution of propargyl bromide (22 mmol) in 10 mL of THF was quickly added. Stirring was maintained for additional 30 min then water and diethylether were poured. The orange aqueous phase was extracted with diethylether and the yellow organic phase was washed with water, dried on Na_2SO_4 and concentrated. The orange oil was dissolved in acetonitrile and rinsed with petroleum spirit then acetonitrile was removed to obtain an orange oil yield (>90%). Despite the unusual orange colour, ^{1}H NMR spectra unravelled a clean compound corresponding to spectroscopic data already reported in literature.[4] Due to it poor stability the product was engaged in the next step without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.51 (1H, s); 6.96 (2H, m); 4.66 (2H, d, J = 2.5 Hz); 2.45 (1H, t, J = 2.5 Hz).



5

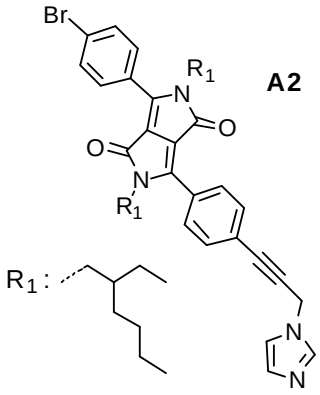
Antenna A1

Compounds **1** (0.3 mmol) and **5** (0.6 mmol) were solubilized in a mixture of distilled dichloromethane/methanol (28 mL, 1/1) and triethylamine (28 mmol). The resulting mixture was degassed by N_2 bubbling under sonication (15 min.). Triphenylarsine (0.8 mmol) and $Pd_2(dba)_3.CHCl_3$ (0.04 mmol) were added and the solution was heated under an argon atmosphere at 40°C for 16 h. Solvents were removed and the resulting solid was purified on column chromatography eluted with the solvent mixture starting with dichloromethane/ethyl acetate (6/4) until pure ethyl acetate to furnish **A1** as a red solid (0.1 g, 75%). ^{1}H NMR (300 MHz, $CHCl_3$) δ_H 7.76 (1H, br s), 7.57 (2H, d, J = 8.1 Hz), 7.29 (2H, d, J = 8.1 Hz), 7.15 (2H, br s), 5.02 (2H, s), 2.53 (6H, s), 2.29 (4H, q, J = 7.5 Hz), 1.25 (6H, s), 0.98 (6H, t, J = 7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ_c 154.2, 138.8, 138.1, 136.9, 136.8, 133.0, 132.4, 130.5, 129.8, 128.7, 122.1, 118.9, 85.6, 82.8, 37.3, 17.1, 14.6, 12.6, 11.9. MALDI-TOF: m/z: Calcd for: 483.2641 [M (^{10}B)]$^+$, Found: 483.2649 [M(^{10}B)]$^+$, Δ = 1.7 ppm.



Antenna A2

Compounds **2** (0.07 mmol), **5** (0.08 mmol) and CuI (0.005 mmol) were solubilized in anhydrous toluene (5 mL) under an argon atmosphere. Triethylamine (9.0 mmol) was then added and the mixture was degassed by N_2 bubbling under sonication (15 min). $Pd(PPh_3)_4$ (0.007 mmol) was added and the solution heated to 50°C for one night. Solvent was then removed under vacuum and the crude reaction miwture was purified on silicagel column chromatography with pure dichloromethane. The remaining starting material was eliminated and polarity of the eluent was then increased with MeOH until the composition 98/2. Orange fractions were gathered and the solvents were removed toafford **A2 as** an orange-red solid (0.02 g, 40%). ^{1}H NMR (300 MHz, $CHCl_3$): δ_H 7.72 (3H, br d, J = 8.3 Hz), 7.60 (4H, s), 7.51 (2H, d, J = 8.3 Hz), 7.13 (2H, br s), 5.00 (2H, s), 3.68 (4H, m), 1.42 (2H, m), 1.15-1.05 (16H, m), 0.80-0.75 (6H, m), 0.72-0.65 (6H, m). ^{13}C NMR (75 MHz, CDCl3): δ_c 162.6, 147.9, 147.8, 132.2 (br), 130.2, 128.9, 128.7, 128.5, 127.3, 125.7, 124.4, 110.2, 110.0, 85.7, 84.3, 45.1, 38.6, 37.6, 30.4, 28.3, 23.8, 23.0, 14.1, 10.5. MALDI-TOF: m/z: Calcd for: 695.2955 [M+H]$^+$, Found: 695.2924 [M+H]$^+$, Δ = 4.5 ppm.



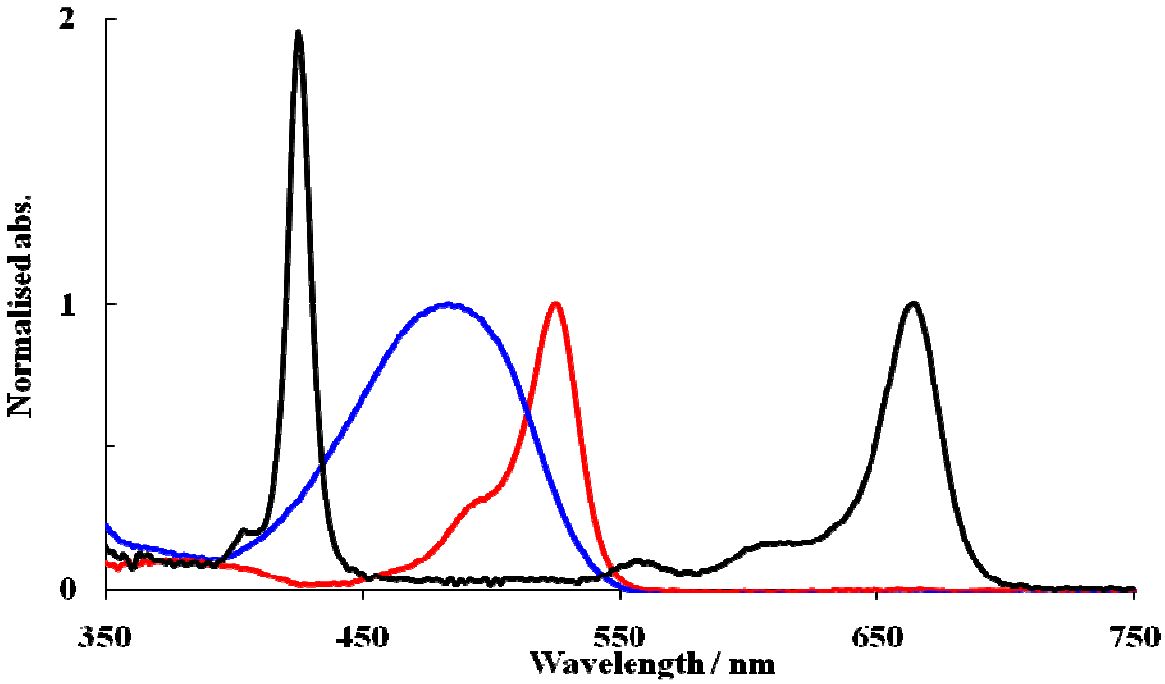


Figure S1. Overlay of the normalized absorption spectra of **D** (black), **A1** (red) and **A2** (blue) recorded in THF solution

Table S1. Electronic properties of **A1**, **A2** and **D** recorded in THF. [a]calculated with the equation $E_{00} = 1240/\lambda_{inter}$, with λ_{inter} = wavelength at the intersection of the absorption and emission spectra.

Dye	λ_{max} (nm)	ε (L.mol^{-1}.cm^{-1})	λ_{max} (nm) on TiO_2	$\lambda_{em\ max}$ (nm)	[a]E_{00} (eV)
A1	**525**	**(0.53*10^5)**	**531**	**541**	**2.33**
A2	**484**	**(0.13*10^5)**	**494**	**552**	**2.36**
D	**425** **664**	**(2.90*10^5)** **(1.72*10^5)**	**432** **666**	**675**	**1.85**

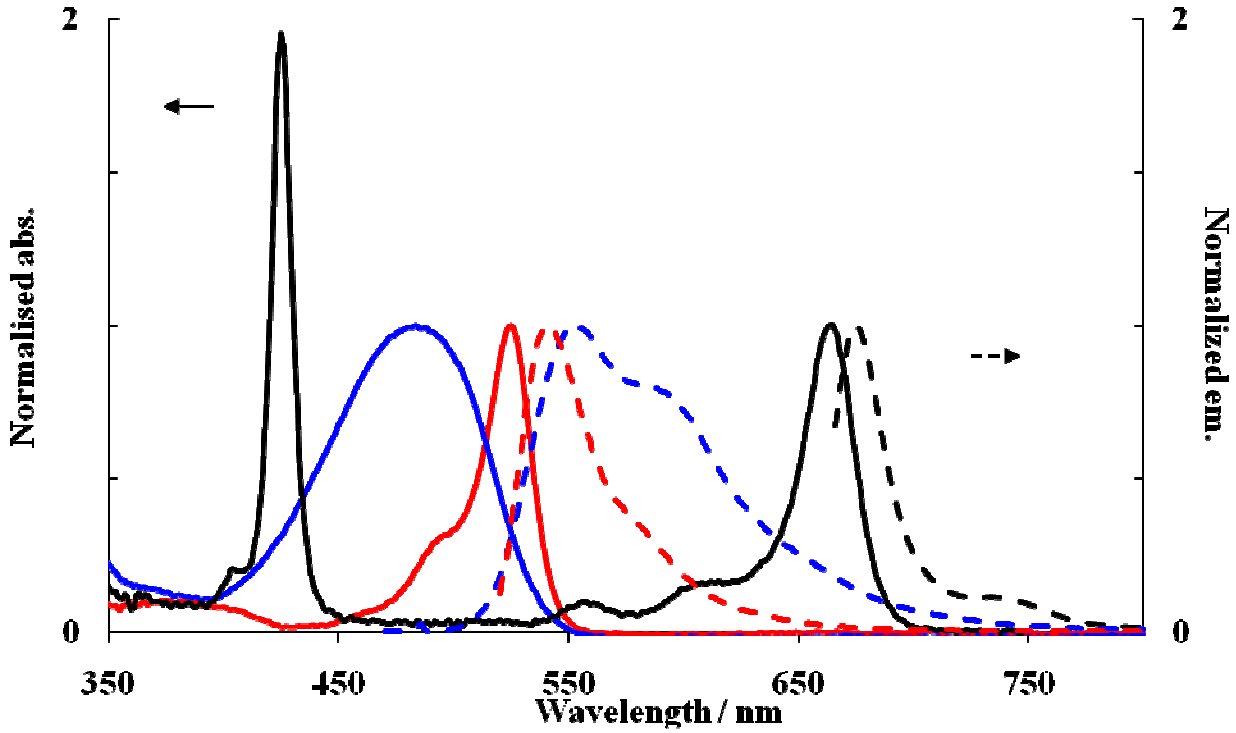


Figure S2. Normalized absorption (solid line) and emission (dashed line) spectra of **D** (black line; excitation at 664 nm), **A1** (red line; excitation at 525 nm) and **A2** (blue line; excitation at 484 nm) in THF.

Table S2. Photovoltaic performances of DSSCs coated with the antennas **A1** or **A2** only (1 h of dipping in THF at 0.2 mM).

Dye	*Voc* (mV)	*Jsc* (mA/cm²)	*ff* (%)	*η* (%)
A1	**405**	**0.85**	**65**	**0.22**
A2	**495**	**1.86**	**71**	**0.65**

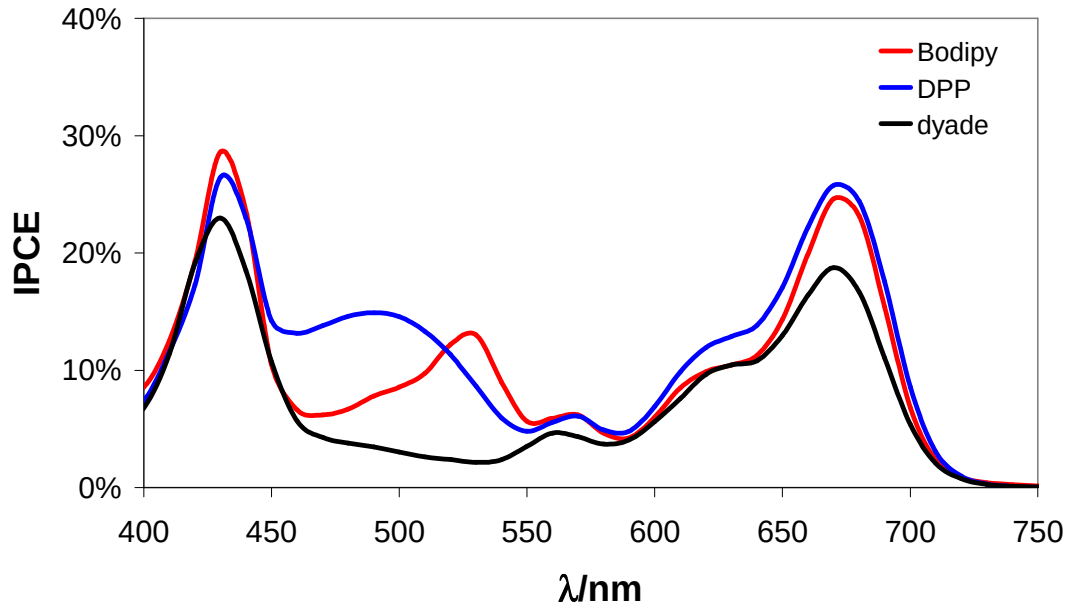


Figure S3. Photoaction spectra of **D** (black line); **D** dipped in a THF bath containing: **A1** (red line) or **A2** (blue line) for 1 h (0.2 mM). Thickness of TiO_2 electrode: 4 μm.

Table S3. Photovoltaic performances as a function of the dipping time of the antenna in THF solution

Dye	*Time of contact between the cell and the antenna (h)*	*Voc (mV)*	*Jsc (mA/cm²)*	*ff (%)*	*η (%)*
D	**/**	**545**	**9.25**	**72**	**3.64**
D[1]	**1**	**525**	**8.08**	**71**	**3.03**
A1	**0.5**	**565**	**9.67**	**72**	**3.94**
	1	**565**	**8.45**	**73**	**3.49**
	2	**535**	**8.00**	**72**	**3.09**
A2	**0.5**	**535**	**9.82**	**73**	**3.81**
	1	**565**	**9.47**	**73**	**3.91**
	2	**535**	**8.53**	**72**	**3.26**

[1]: cells were dipping for 1 h in an antenna free THF bath.

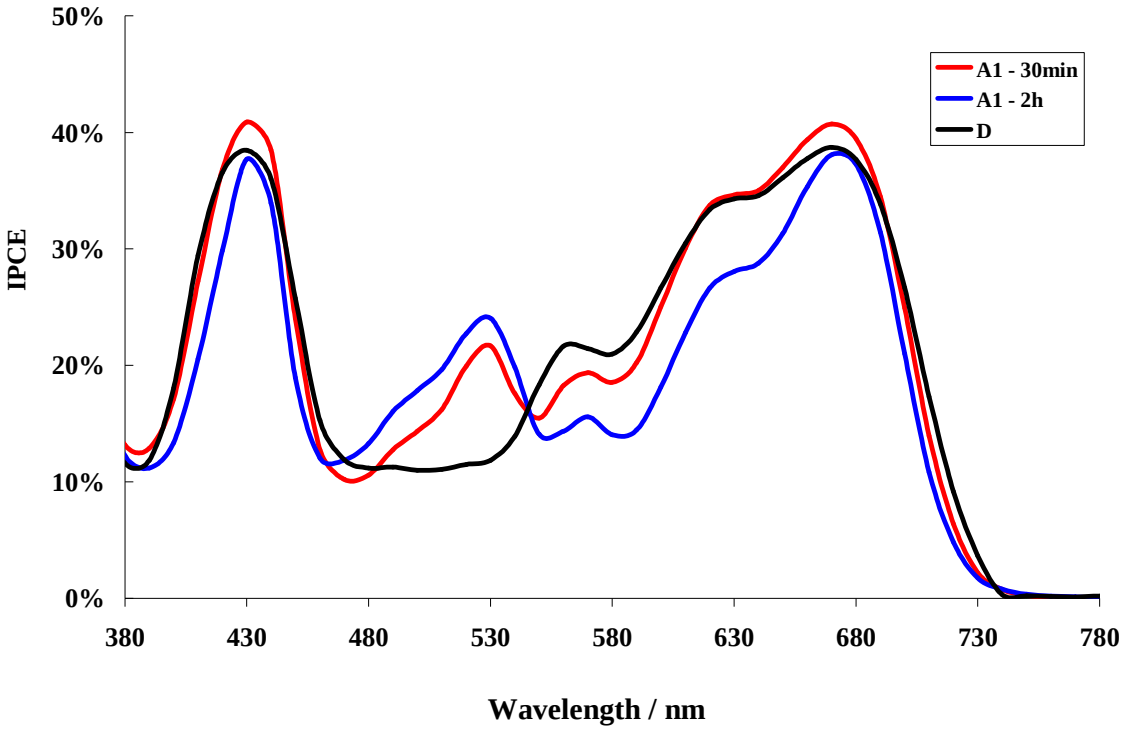


Figure S4. Photoaction spectra of **D** (black trace) and **D** dipped in a THF solution containing: **A1** (0.2 mM) for 30 min (red trace) and for 2 h (blue trace)

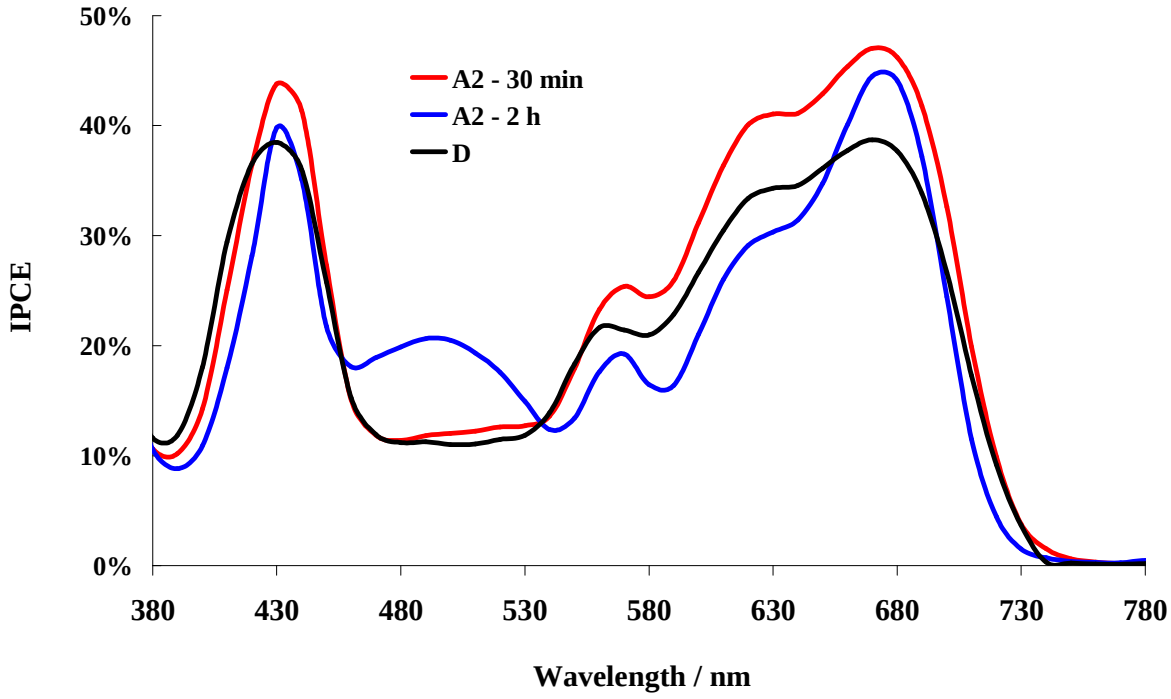


Figure S5. Photoaction spectra of **D** (black trace) and **D** dipped in a THF solution containing: **A2** (0.2 mM) for 30 min (red trace) and for 2 h (blue trace)

Table S4. Photovoltaic performances of the DSSCs coated with **D** + **A1** according to the solvent used to prepare the supramolecular assembly (1 hour of contact of the solution with the photoanode).

Solvent	*Voc* (*mV*)	*Jsc* (*mA/cm²*)	*ff* (%)	*η* (%)
$CHCl_3$	565	5.64	70	2.22
THF	555	8.68	76	3.66
ACN	575	9.71	73	4.10

Table S5. Photovoltaic performances of the DSSC upon ageing (dipping time = 0.5 h in THF). Electrolyte composition: 0.6 M 1,2-dimethyl-3-butylimidazolium iodide, 0.1 M LiI and 0.05 M I_2 in acetonitrile.

Dye	*Time of contact between cell and electrolyte*	*Voc* (*mV*)	*Jsc* (*mA/cm²*)	*ff* (%)	*η* (%)
D	t0 ≈ 1 h	545	9.25	72	3.64
	t0 + 5 days	545	8.88	72	3.47
A1	t0 ≈ 1 h	565	9.67	72	3.94
	t0 + 5 days	565	8.44	71	3.36
A2	t0 ≈ 1 h	535	9.82	73	3.81
	t0 + 5 days	545	8.95	73	3.54

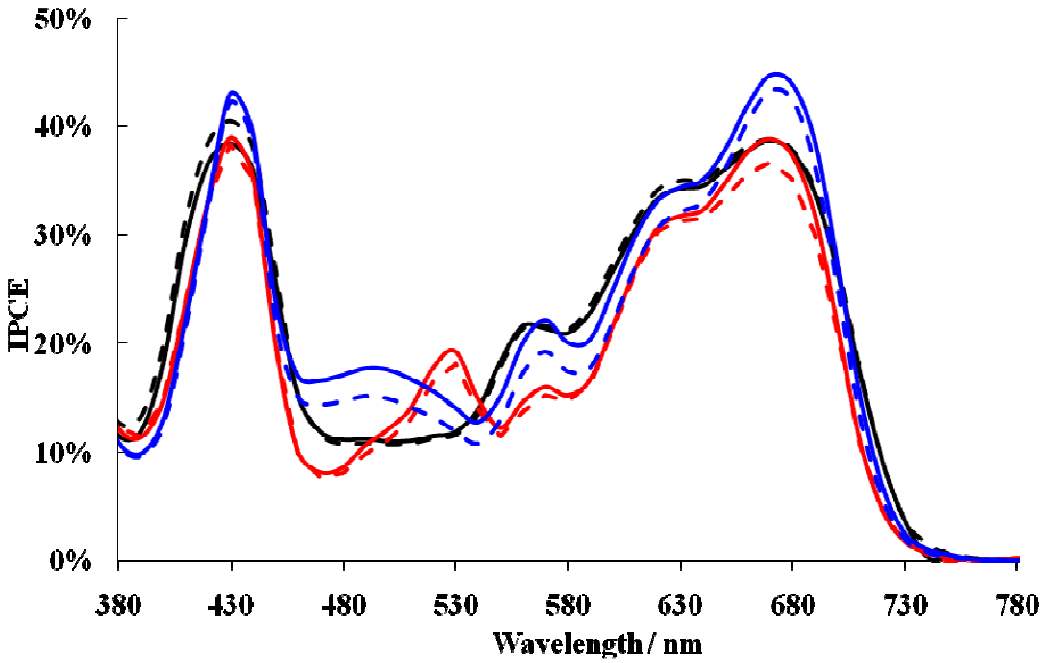


Figure S6. Photoaction spectra of the **D** only (black line); **D** associated with **A1** (red line) or with **A2** (blue line) after 1 h (solid line) and after 5 days later (dashed line). Electrolyte composition: 0.6 M 1,2-dimethyl-3-butylimidazolium iodide, 0.1 M LiI and 0.05 M I_2 + antenna in acetonitrile except for the black traces.

Determination of the amount of D chemisorbed on the TiO_2 film:

The difficulty for the estimation of the number of moles of **D** chemisorbed on TiO_2 film was linked to the degradation of the latter in basic conditions (usually used to desorb the anchored dye on TiO_2). Therefore, we first measured the molar extinction coefficient of the degraded dyad **D** by exposing it to a tetrabutylammonium hydroxide THF solution. The new species (**D'**) exhibited an extinction coefficient of 3.4×10^5 $L.mol^{-1}.cm^{-1}$ at 436 nm. Then, we dipped in the same conditions a TiO_2 electrode initially coated with **D**. The electrode quickly bleached and the absorbance of the resulting yellow solution was measured by UV-visible spectrometry. Around 13 nmol of **D** were detected for a cell of 0.25 cm^2, that is to say 5.2×10^{-8} $mol.cm^{-2}$.

References:

1. J. Warnan, F. Buchet, Y. Pellegrin, E. Blart and F. Odobel, *Org. Lett.*, 2011, **13**, 3944-3947.
2. A. Burghart, H. Kim, M. B. Welch, L. H. Thoresen, J. Reibenspies, K. Burgess, F. Bergstroem and L. B. A. Johansson, *J. Org. Chem.*, 1999, **64**, 7813-7819; T. N. Singh-Rachford, A. Haefele, R. Ziessel and F. N. Castellano, *J. Am. Chem. Soc.*, 2008, **130**, 16164-16165.
3. E. Q. Guo, P. H. Ren, Y. L. Zhang, H. C. Zhang and W. J. Yang, *Chem. Commun.*, 2009, 5859-5861; G. Zhang, K. Liu, Y. Li and M. Yang, *Polym. Int.*, 2009, **58**, 665-673.
4. A. Casaschi, R. Grigg and J. M. Sansano, *Tetrahedron*, 2001, **57**, 607-615.