## **Supplementary Information**

Synthetic analogues of anthocyanins as sensitizers for dye-sensitized solar cells.

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## 1. General synthetic scheme for the synthesis of the flavylium salts used

Scheme S1 – Synthetic startegy for the obtention of the flavylium salts used in this work: aldol condensation between substituted 2-hydroxyaldehydes and substituted acetophenones under acidic condition.

## 2. Thermodynamics and kinetics of 7-(N,N-diethylamino)-3',4'-dihydroxyflavylium

Similarly to other aminoflavylium derivatives,<sup>1</sup> the compound 7-(N,N-diethylamino)-3',4'dihydroxyflavylium is involved in a series of chemical equilibria as shown in Scheme S1.



Scheme S1. Network of chemical reactions for 7-(N,N-diethylamino)-3',4'-dihydroxyflavylium in aqueous solution.

The thermodynamics and kinetics of 7-(*N*,*N*-diethylamino)-3',4'-dihydroxyflavylium chloride were studied in 50:50 (V/V) ethanol:water. The absorption spectrum of the compound 7-(*N*,*N*-diethylamino)-3',4'-dihydroxyflavylium after a pH jump from equilibrated solutions at pH=1.05 to higher pH values (direct pH jumps) followed by stopped flow are shown in Fig. S1. When the absorption spectra are taken after 4 ms, the variations are compatible with an acid-base equilibrium between AH<sup>+</sup> and A, with p $K_a$ =7.0. However, after 5 s, the absorption spectra at higer pH values are not coincident with those of the quinoidal base, see Fig. S1B. Indeed, the kinetic trace at 613 nm between 4 ms and 5 s is best fitted with a biexponential law, Fig. S1C. The faster process in Fig. S1C corresponds to a decrease in absorbance at 613 nm and can be attributed to the hydration reaction while the slowest process, corresponding to an increase of the absorbance, is due to the tautomerization reaction to form  $Cc(Cc^{-})$ . The increased absorption in the visible of this last species for higher pH values is one indication that  $Cc^{-}$  should be formed, at least partially.<sup>2</sup> A slower process (not shown in this picture) can be observed for longer times, corresponding to the *cis-trans* isomerization. Actually, the state after 5 s can be considered as a pseudo-equilibrium involving all the species except Ct.



**Figure S1. A** - Absorption spectra of 7-(*N*,*N*-diethylamino)-3',4'-dihydroxyflavylium monitored by stopped flow 4 ms upon a pH jump from pH=1.05 (equilibrated solution, 50% EtOH;  $1.4 \times 10^{-5}$ M) to higher pH vales; inset: fitting of the absorbance at 607 nm leads to  $pK_a=7.0$ ;  $\varepsilon_{AH+}(550 \text{ nm})=33000 \text{ M}^{-1}\text{ cm}^{-1}$ ; **B** - the same after 5 s; the point-trace line, corresponding to the normalized spectrum after 4 ms at the highest pH, is included for comparison purposes; **C** - kinetic trace between 4 ms and 5 s at 613 nm.

The absorption spectra of the equilibrated solutions are shown in Fig. S2. The data are compatible with an equilibrium between flavylium cation (acidic species) and the global CB species, containing essentially the *trans*-chalcone. At more basic pH values, the absorption spectrum of the ionized *cis*-chalcone appears. From the ratios  $\frac{K_a}{K'_a}$  and  $\frac{K_b(1+K_t)}{K'_a}$ , respectively the mole faction of the quinoidal base and the sum of B and Cc are expected to be 0.6% and 0.8%.

Protonation of the amine in position 7 of the flavylium cation is extremelly difficult as observed in other similar compounds, see Fig. S2B.<sup>1</sup>



**Figure S3. A** - The same set of solutions as in Fig. S2, after equilibration (48h in the dark); inset: fitting of the absorbance at 440 and 550 nm leads to  $pK'_a=4.83$ ; **B** – At very low pH values, protonation of the flavylium cation at the amine substituent leads to the blue-shifted N<sup>+</sup>AH<sup>+</sup> species; inset: fitting of the absorbance at 550 nm yields  $pK_a(N^+AH^+)=-0.76$  ( $K_a=5.8$ ).

The following energy level diagram regarding the thermodynamics of the system is shown in Scheme  $2.^{3}$ 



Scheme 2. Energy diagram of 7-(N,N-diethylamino)- 3',4'-dihydroxyflavylium system in acidic medium.

## References

<sup>&</sup>lt;sup>1</sup> M. C. Moncada, D. Fernández, J. C. Lima, A. J. Parola, C. Lodeiro, F. Folgosa, M. J. Melo, F. Pina' Org. Biomol. Chem., **2004**, 2, 2802-2808.

<sup>&</sup>lt;sup>2</sup> Unprotonated chalcones are always red shifted in comparison with the neutral ones.

<sup>&</sup>lt;sup>3</sup> F. Pina, M. J. Melo, C. A. T. Laia, A. J. Parola, J. C. Lima, *Chem. Soc. Rev.*, **2012**, *41*, 869-908.