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Engineered co-sensitization system for highly efficient dye solar cells[†]

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Novel co-sensitizers have been structurally tailored and implemented in a multi-sensitized devices demonstrating a synergic efficiency enhancement attributable to improved light-harvesting as well as prevention of charge recombination.

Dye-sensitized solar cells (DSSC) still represent to date the most suited candidate for the next generation of building integrated photovoltaics because of their peculiarity in terms of transparency and coloration which paves the way to novel applications. Aiming at improving the DSSC performances, substantial efforts have been devoted to the search for new and efficient fully-organic dyes, providing advantages in terms of the molecular design flexibility and higher molar extinction coefficients with respect to their inorganic counterparts.[1-3] In order to overcome the light-harvesting limits of organic sensitizers due to their narrower absorption bands, co-sensitization (employing multiple dyes with complementary absorption features) has recently emerged as a cunning approach to achieve a panchromatic optical response. It has already been shown that the co-deposition of two or more dyes lead to an improvement of the power conversion efficiency with respect to that attainable by the individual sensitizers.[4] At the same time, however, apart from a broadly extended absorption spectrum, the structure of an optimal sensitizer should also prevent recombination effects due to aggregation or stacking when adsorbed onto the inorganic semiconductor surface. If this criterion is not met, the co-adsorption of an additive is again an appropriate remedy. An additive performs its favourable task by *i)* occupying the voids between the dye molecules, thus reducing charge recombination effects and by *ii)* assisting their packing on the TiO_2 surface avoiding aggregation. The examples of co-sensitization reported thus far have concentrated on the choice of the suitable co-adsorbents for the use in mixture with well-known high-performing dyes (porphyrins,[5] Ru-based complexes[6] or organic sensitizers[7]) without any evident structural correlation between the main sensitizer and the relevant co-adsorbent.
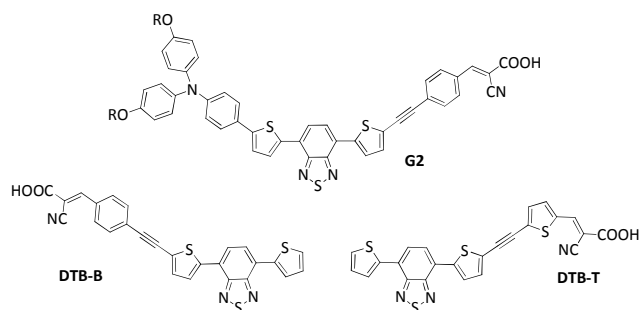

Fig. 1 Chemical structures of the main sensitizer **G2** and co-adsorbent **DTB-B** and **DTB-T** (R = 2-ethyl-hexyl).

In this work, we aim at demonstrating that the DSSC performances of largely π-extended sensitizers can be noticeably improved by co-deposition with a structurally analogous dye, providing a guideline for the selection of the dyes pair for suitable co-sensitization.

In the framework of our studies on novel organic dyes for DSSCs, we have recently embarked in the synthesis of **G2**[8] (Fig. 1), a sensitizer which was devised with an unusually extended benzothiadiazole-based π-bridge. The UV-vis spectrum of **G2**, as commonly observed for benzothiadiazole-based dyes,[9] is characterized by a "camelback" profile (Fig. 2), which leads to an absorption lacuna between 400 and 500 nm. Corroborated by DFT calculations and taking **G2** as starting structure, we have designed the co-sensitizers **DTB-B** and **DTB-T** (Fig. 1), that were endowed with i) a good absorption between 400 and 500 nm; ii) a suitable size to improve their co-deposition on the semiconductor surface; *iii)* conformational prerogatives to hamper molecular aggregation during the co-deposition. Removing the triarylamine donor from the structure of **G2** seemed as the simplest strategy to suitably increase the energy-gap of the relevant structures consequent to a remarkable lowering of the theoretical HOMO energy level of **DTB-B** and **DTB-T** with respect to **G2** without remarkably affecting their LUMO energy level (see Fig.S1). The calculated HOMO and

LUMO levels guarantee the feasibility of the charge transfer processes in the DSSC device and hint complementary absorption spectra with respect to that of **G2** as can clearly be evidenced comparing their simulated absorption spectra in Fig. S2. Owing to the presence of ethynylene moiety, the optimized geometry of **DTB-B** and **DTB-T** was found to be near planar, potentially favouring its co-adsorption into the interstitial sites left by a bulkier sensitizer on TiO$_2$ (Fig. S3). Furthermore, although deprived of a formal electron-donating group, the photo-excitation dynamics (simulated by their natural transition orbitals, Fig. S4) allows to hypothesize a partial shift of the electron density towards the anchoring portion of the molecule consequent to the photo-excitation, thus favouring the electron transfer in the course of the DSSC work cycle. The synthesis of **DTB-B** and **DTB-T** was carried out as described in the ESI. The products have been synthesized and characterized by elemental analyses, NMR, HR-MS, IR and cyclic voltammetry. The main sensitizer **G2**, shows two absorption bands at 373 nm (ε = 23200 M^{-1}cm^{-1}) and 538 nm (ε = 20000 M^{-1}cm^{-1}), Notably, the synthesised co-sensitizers show their main absorption peak at 471 nm (ε = 17000 M^{-1}cm^{-1}, **DTB-B**) and 475 nm (ε = 14500 M^{-1}cm^{-1}, **DTB-T**) nicely falling (Fig. 2) between the two absorption band recorded for **G2**.

Next, the photovoltaic performances of the fully-organic multi-sensitizer systems have been investigated. To this purpose, DSSC devices were constructed from TiO$_2$ photo-anodes co-sensitized with appropriate mixtures of **G2** and either **DBT-B** or **DTB-T** comparing the results with those obtained from devices embodying each of the single sensitizers. After the suitable screening (see Table S1) of the blend composition, it was found that the best results for the co-adsorption are obtained with a **G2**/ **DBT-B** (**DTB-T**) molar ratio of 2/1. Table 1 summarizes the open-circuit voltage (V$_{OC}$), short-circuit photocurrent density (J$_{SC}$), fill factor (FF), and power conversion efficiency (η), extracted from the photocurrent density-voltage (J-V) curves of the most representative devices. The PCE of devices A, B and C (based on **G2**, **DTB-B** and **DTB-T**) were 5.58%, 1.10% and 1.80%, respectively, whereas the performances of the co-sensitized devices D and E (which correspond to **G2/DTB-B** and **G2/DTB-T** systems) resulted in a conspicuous enhancement of the performance (6.22% and 7.84%, respectively) with respect to device A. Since the V$_{oc}$ and FF values are very similar in devices A, D and E, the increase is mainly due to the higher photocurrent in the co-sensitized devices (13.86 and 15.33 mA/cm^2 for devices D and E, respectively). The dye loading of devices (mole of adsorbed dye *per* cm^2 of TiO$_2$,

Fig. 2 (Left) Normalized absorption spectra of **G2**, **DTB-B** and **DTB-T** recorded in THF. (Right) IPCE spectra of devices A-E (see table 1).

Table 1 Photovoltaic parameters of devices based on individual dyes **DTB-B**, **DTB-T** and **G2** as well as co-sensitized devices measured under 1.0 sun illumination (AM 1.5, 100 mW/cm^2).

Device	Dye	J$_{SC}$ [mA/cm^2]	V$_{OC}$ [V]	FF	η [%]	Dye loading[b]
A	**G2**	11.39	0.70	0.70	5.58	2.1
B	**DTB-B**	2.86	0.54	0.71	1.10	3.4
C	**DTB-T**	4.02	0.58	0.77	1.80	3.2
D	**G2/DTB-B**[a]	13.86	0.67	0.67	6.22	1.7/1.3
E	**G2/DTB-T**[a]	15.33	0.71	0.72	7.84	1.8/1.5

[a]2/1 molar ratio; [b] [10^{-7} mol/cm^2].

Table 1) was estimated by UV-vis after dye desorption in alkaline solution (see ESI). The lower surface concentration of **G2** in device A (2.1 × 10^{-7} mol/cm^2) with respect to that of **DTB-B** and **DTB-T** dyes (3.4 × 10^{-7} and 3.2 × 10^{-7} mol/cm^2, in devices B and C, respectively) can be ascribed to the higher steric hindrance of the triarylamine containing **G2**. Dye desorption also allowed an estimate of the loading of individual dyes in co-sensitized photo-anodes D and E**.** A lower uptake for the individual sensitizers was estimated, however, the total dye loading was 3.0 × 10^{-7} and 3.3 × 10^{-7} mol/cm^2 for devices D and E, respectively, which is comparable to the result obtained for device B and C, suggesting that the TiO$_2$ surface coverage obtained with co-sensitization was complete. These results indicate that, when adsorbed onto the titania surface, **G2** leaves enough space to allow the co-adsorption of the smaller and highly planar **DTB-B** or **DTB-T** dyes. The device characterization was completed by measuring the incident photon-to-current conversion efficiency (IPCE) spectra, shown in Fig. 2b. The photo-response of the **G2**-based device clearly evidences a drop at ~450 nm (corresponding to the absorption minimum recorded in the UV spectrum) which conversely could not be observed in the IPCE spectra of the co-sensitized devices D and E, due to the absorption of **DTB-B** and **DTB-T** dyes at ~450 nm. However, the sole light-harvesting effect is not sufficient to justify the above referred enhancement of the photocurrent density. The question is, therefore, shifted on the role of the dyes arrangement onto the TiO$_2$ surface in the increasing of the photovoltaic performances.

In order to experimentally address this issue, both electrochemical charge capacitance and charge transfer resistance at the TiO$_2$/dye/electrolyte interface have been measured for all devices by electrochemical impedance spectroscopy (EIS).[10] Figure 3 shows the measured capacitance (C$_{meas}$) and the charge transfer resistance (R$_{CT}$) as a function of corrected voltage. Consistently with the recorded photocurrent density values, the highest C$_{meas}$ (indicating the amount of photo-generated electrons injected in TiO$_2$ conduction band) was observed for devices D and E, confirming the advantages brought about by the co-sensitization process. This result can be justified by admitting a combined effect of the reduced dye aggregation due to the presence of the co-sensitizer as well as to its contribution to the enhanced light-harvesting. Charge-transfer resistance (Fig 3) was
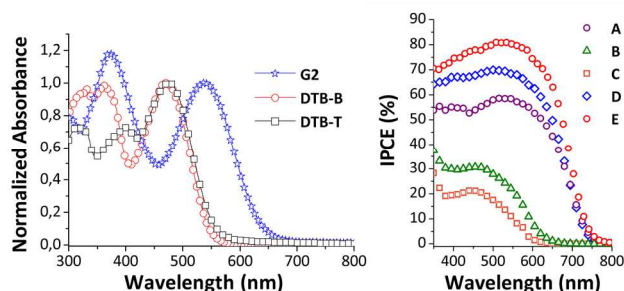
also affected by the nature of the sensitizers; the co-sensitized device E showed higher recombination resistance with respect to the

devices A-C. In fact, the co-sensitization of **G2** with **DTB-T** resulted
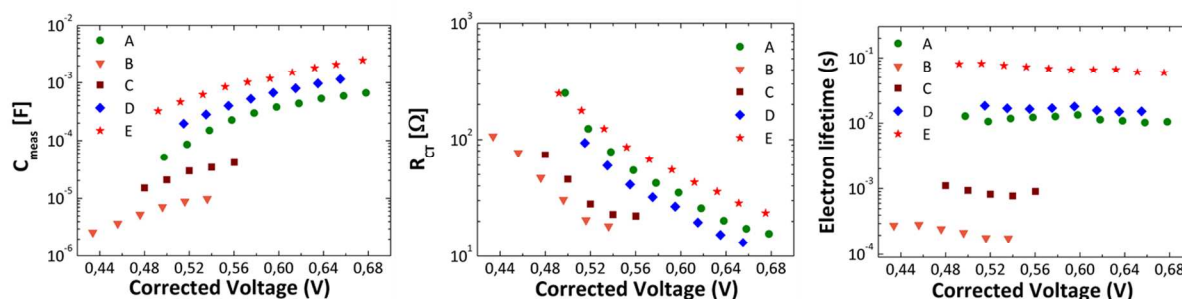

Fig. 3 Measured capacitance (left), charge transfer resistance (middle) and apparent electron lifetime (right) as a function of the corrected voltage for the devices A-E.

not only in an increase of injected electrons in the TiO_2 conduction band, but also in a drop in charge recombination at the TiO_2/electrolyte interface, as testified by the higher V_{OC} of device E. A different behaviour was observed for device D, which showed a lower R_{CT} value with respect to devices A and E, indicating that the **G2/DTB-B** co-sensitization is less efficient than the **G2/DTB-T** one in terms of recombination hindrance, in spite of its good photo-generated electrons injection ability. Eventually, the electron lifetime (τ_n) was calculated by the equation $\tau_n = R_{CT}C_\mu$.[11] The trend defined by the values of the electron lifetime, shown in Fig. 3, follows the one revealed by the photovoltaic measurements. The higher electron lifetime observed for device E demonstrates that the **G2/DTB-T** co-sensitization lead to an effective suppression of the recombination phenomena, probably due to the formation of a more compact dye layer uniformly covering the TiO_2 surface, thus reducing detrimental recombination between transferred electrons and triiodide acceptor.

In conclusion, we have developed a novel co-sensitization system which allows to simultaneously reduce the intermolecular quenching phenomena across the anchored dyes as well as to maximize the light harvesting capabilities of the photoelectrode. This unprecedented engineering of the co-adsorbents seems to induce a full synergy with the relevant main sensitizer, leading to photovoltaic performances higher than the sum of the corresponding individual component devices.

Notes and references

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