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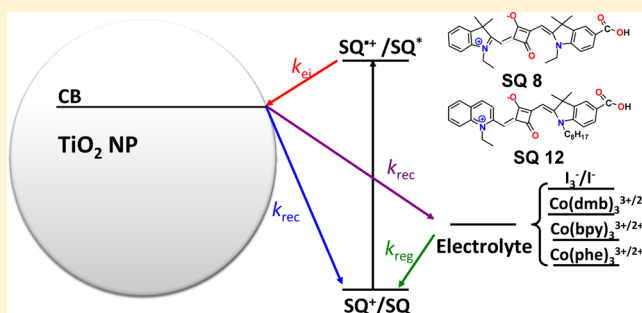
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S Supporting Information

ABSTRACT: A series of dye-sensitized solar cells (DSSCs) has been prepared by using indole-based or quinoline-based squaraines (SQs) as the sensitizer and containing the commonly used I_3^-/I^- redox pair or the lately employed cobalt complexes, $[Co(dimethylbipyridine)_3]^{3+/2+}$, $[Co(bipyridine)_3]^{3+/2+}$, and $[Co(phenanthroline)_3]^{3+/2+}$ redox electrolytes. The photodynamics of the different electron transfer reactions have been investigated by means of the femto- to millisecond pump–probe techniques. In the femtosecond transient absorption experiments, the electron injection rate constants and efficiencies, k_{ei} and ϕ_{ei} , were determined for each cell. Larger values of k_{ei} and ϕ_{ei} for the indole-based (SQ 8) compared to the quinoline-based (SQ 12) squaraines were obtained ($13.2 \times 10^{10} s^{-1}$ and 0.95×10^{10} vs $6.9 \times 10^{10} s^{-1}$ and 0.81 for SQ 8 or SQ 12 with the I_3^-/I^- pair, respectively), despite the similar values of the electron injection driving forces ($-\Delta G^0_{ei} = 0.75$ vs 0.76 eV). This is due to the lower electron density in the lowest unoccupied molecular orbital at the anchoring group ($-COOH$) in SQ 12 compared to SQ 8. However, the type of electrolyte did not affect the kinetics of the electron injection processes. In the flash photolysis experiments, the kinetic parameters of the electron recombination via dye or electrolyte and the cation regeneration were calculated from the decays of the transient absorption signals of the electrons (1550 nm) or the SQ cation (570 nm). It was found that the electron recombination with the oxidized redox species is faster with the Co-based compared to the I_3^-/I^- electrolytes for both SQs, $\tau_{rec} = 3$ versus ~ 0.5 –1 ms. This proves that the steric hindrance in these SQs is not sufficient to avoid the approach of the Co^{3+} species to the surface of the TiO_2 nanoparticle. Moreover, the regeneration rate constants and efficiencies, k_{reg} and ϕ_{reg} , are considerably smaller for the cells with the different Co-based electrolytes compared to those with the I_3^-/I^- pair (i.e., $k_{reg} = 30 \times 10^4$ vs $8 \times 10^4 M^{-1}s^{-1}$ and $\phi_{reg} = 0.96$ vs 0.75 with the $[Co(dmb)_3]^{3+/2+}$ for SQ 8). This is explained by the lower regeneration driving force, $-\Delta G_{reg}$, in the Co-based electrolytes (0.3–0.1 eV). Thus, the use of Co-based electrolytes in these two SQs is detrimental to the overall efficiency of the cell, since $-\Delta G_{reg}$ values below 0.4 eV do not give complete regeneration efficiency. Finally, we have compared the measured photocurrent with the calculated electron injection and regeneration efficiencies, and we found a good correlation between both parameters.



1. INTRODUCTION

The functioning mechanism of dye-sensitized solar cells (DSSCs) involves a complicated set of electron transfer reactions working together to generate photocurrent from the solar energy harvesting. Characterization of these reactions is a crucial condition to shed some light on the different values of efficiencies found in the literature due to the wide range of used dyes, electrolytes, additives, or semiconducting nanoparticles.^{1–3} Among the vast arsenal of characterization techniques utilized in the field of DSSCs, the importance of the pump–probe absorption and emission spectroscopies has been demonstrated to get details on the photodynamics involved in the photoelectrical circuit.^{4–6} Thus, thanks to the development of femtochemistry,⁷ several works have been oriented to understand the relationship between the efficiency and the

photocurrent of the cells, while characterizing the values of the involved photoreaction rate constants.^{8–10} Although the relationship is not easy to get, information on the photodynamical cycle helps in understanding important aspects of the DSSC working scheme. This in turn leads to better design of the various building blocks of the DSSC, such as the dyes, the semiconductor, and the electrolytes.

Squaraines, SQs, are red-absorbing dyes that are growing in importance as model compounds of near-IR (NIR) dyes in DSSCs.^{11–18} Several works have reported on the photodynamics of SQs embedded on TiO_2 nanoparticles, showing an

Received: February 7, 2013

Revised: April 23, 2013

Published: May 14, 2013

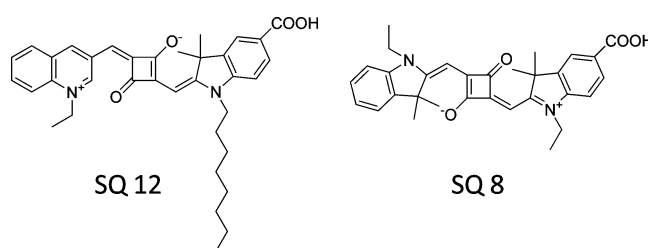


ultrafast electron injection (from hundreds of femtoseconds to a few picoseconds) and a relatively fast regeneration of the SQ cation, SQ^{+} , formed after the electron injection.^{19–24} Recently, we have reported on the femto- to millisecond behavior of a family of four SQs (symmetric or asymmetric, with different substituent groups),^{22,23} as sensitizers in DSSCs. The main conclusions of these studies can be summarized as follows: (1) we observed a faster electron injection reaction in asymmetric SQs due to the unidirectional flow of electrons and (2) a faster dye regeneration process in SQs possessing an electron-accepting substituent, explained in terms of a larger positive charge on the SQ backbone that promotes the approach of the reducing agent, I^- . However, the studied SQ-based DSSCs showed a relatively low overall efficiency, far from their theoretical maximum power conversion. Thus, to increase the extracted photocurrent and the overall efficiency, it is necessary to extend the studies of the photodynamics to other SQs with some structural variations. Therefore, a more extensive knowledge about the influence of the chemical modifications on the efficiency of the solar cells will help in the design of optimized structure of the SQs.

The two classical approaches improving the efficiency of the DSSCs are the extension of the sensitizer absorption to the NIR in order to extract more photocurrent and the increase of the open circuit voltage (V_{oc}), which is directly depending on the redox energy potential of the electrolyte.^{25,26} The latter energy is fixed at -4.9 V for the most commonly used redox electrolyte, I_3^-/I^- . Therefore, a good strategy to increase the V_{oc} is the substitution of I_3^-/I^- by another redox pair with the same regeneration properties but with a more negative redox potential. In this respect, a family of cobalt (Co)-based electrolytes with redox potential between 0.1 – 0.3 V more negative than that of I_3^-/I^- have been used as an alternative.²⁷ Moreover, the Co-based electrolytes present additional advantages with regard to the I_3^-/I^- pair: they absorb poorly the visible light and their corrosiveness toward metals is much lower, which helps to extend the stability of the device. However, the main disadvantage of these electrolytes is the faster recombination of the oxidized redox species with the electrons in the TiO_2 nanoparticles, which results in a decrease of the measured photocurrent. To overcome this limitation, the used strategy has been the introduction of bulky groups, both in the sensitizer and in the Co-based electrolytes, to prevent the interaction between the TiO_2 surface and the oxidized redox species.²⁷ This approach yielded power conversion efficiencies of over 12% at 100 mW/cm^2 by using high extinction coefficient dyes, such as porphyrins.²⁸

Herein, we report on the femto- to millisecond characterization of the photocycle involved in complete DSSCs sensitized with two types of SQs and containing I_3^-/I^- or one of the three Co-based electrolytes by using pump–probe techniques. The sensitizers are indole-based (SQ 8) and quinoline-based (SQ 12) squaraines (Chart 1), the latter one having its absorption spectrum shifted to longer wavelengths (from 648 to 663 nm) as a result of the extension of the π conjugation. In the femtosecond (fs) UV–visible transient absorption experiments, we observed a larger electron injection rate constant, k_{ei} , in SQ 8 compared to that using SQ 12 in line with its higher measured photocurrent. This result is explained in terms of a lower electron density contribution in the lowest unoccupied molecular orbital (LUMO) at the $-COOH$ anchoring group in SQ 12. The values of k_{ei} of the same SQ with I_3^-/I^- or with one of the three Co-based electrolytes are

Chart 1. Molecular Structure of the Two Studied SQs



very similar to each other, reflecting that the electrolyte does not affect the electron injection process. In the nano- to millisecond flash photolysis experiments (UV–visible–NIR), we found that the electron recombination with the oxidized redox species was faster for the cells containing the different Co-based electrolytes. This result indicates that the bulky groups of the SQs are not enough to prevent the interaction between the TiO_2 surface and the oxidized redox species. On the other hand, the regeneration rate constants and efficiencies, k_{reg} and ϕ_{reg} , were measured for the different Co-based or I_3^-/I^- redox electrolytes. A smaller value was found for the Co-based redox pairs, which is in line with its lower measured photocurrent. This is explained by the lower driving force for the regeneration process, $-\Delta G_{reg}$, in the Co-based electrolytes.

2. EXPERIMENTAL SECTION

The indole derivative, 2,3,3-trimethyl-3H-indole-5-carboxylic acid, used as the anchoring group for both SQ dyes, was synthesized following the methodology reported by Pham et al.²⁹ The asymmetric SQ 8 was synthesized using the semisquaraine ester *N*-ethyl-indole and *N*-ethyl-indole carboxylic acid as per the method described in our earlier publications.^{30,31} On the other hand, the asymmetric SQ 12 was synthesized from the condensation of a semisquaraine ester of quinoline donor with *N*-octyl-indole carboxylic acid. Details of this synthesis have been recently published.³² The final purity of both SQ dyes was confirmed by high-performance liquid chromatography while structural elucidation was conducted using high-resolution fast ion bombardment mass spectrometry and NMR spectroscopy.

Preparation of the TiO_2 nanoparticle thin films was performed with the Ti-Nanoxide HT paste (Solaronix SA) by using the doctor blade technique with the help of two parallel adhesive Scotch tapes. The substrate was dipped in an ethanol solution (Scharlau, extra pure) containing the SQ dye in presence of chenodeoxycholic acid (CDCA) coadsorber (Sigma–Aldrich, $\geq 97\%$). The SQ dye concentration was fixed at 0.15 mM while the CDCA concentration was 30 mM . The optical density at the maximum of the absorption peak, ~ 640 – 675 nm , was around 1.5 for all the studied cells. To fabricate the complete solar cells, the platinized counter electrode was placed directly on top of the dye-adsorbed TiO_2 nanoparticle electrode and sealed with thermal adhesive films ($25\text{ }\mu\text{m}$ Surlyn, Meltronix, Solaronix) that also act as a separator. The different electrolytes were introduced in the complete cells with an analytical syringe through two holes drilled in the counter electrodes, which were later sealed by a piece of Surlyn and a microscope coverslip.

Cyclic voltammetry was utilized to obtain the oxidation potentials of SQ 8 and SQ 12 and for the different Co-based electrolytes. The oxidation potentials of the SQs were measured in dimethylformamide using ferrocene as the reference

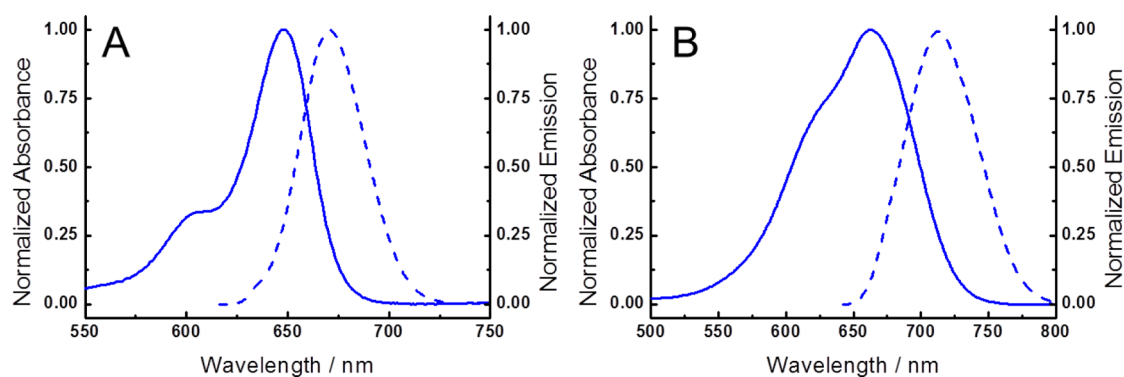


Figure 1. Normalized steady-state visible–NIR absorption (solid lines) and emission (dashed lines) spectra of SQ 8 (A) and SQ 12 (B) based solar cells and containing the I_3^-/I^- electrolyte. The excitation wavelengths were 610 and 625 nm, for SQ 8 and SQ 12, respectively.

compound (0.55 V vs SCE) and 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Two different platinum wires were used as the working and counter electrode while the saturated calomel electrode (SCE) was used as the reference electrode. The voltammetric measurements of the cobalt complexes were performed in acetonitrile (ACN, Sigma–Aldrich, anhydrous 99.8%) solutions containing 0.1 M tetrabutylammonium hexafluoro-phosphate salt (Fluka). A glassy carbon disc electrode, was employed as the working electrode. The counter and reference electrodes were a Pt bar and a Ag/AgCl/NaCl saturated electrode, respectively.

The cobalt(II) complexes $[Co(dimethylbipyridine)_3](PF_6)_2$, $[Co(bipyridine)_3](PF_6)_2$, and $[Co(phenanthroline)_3](PF_6)_2$ were synthesized as described in the literature.^{27,33,34} Briefly, 3.3 equivalents of the desired bidentate ligand (Sigma–Aldrich, 99%) were dissolved with magnetic stirring in a minimal amount of methanol (Sigma, $\geq 99.8\%$). One equivalent of $CoCl_2 \cdot 6H_2O$ (Fluka, $\geq 98\%$) was then added to this mixture, and the solution was stirred at reflux for 2 h. An excess of NH_4PF_6 (Sigma–Aldrich, $\geq 99.99\%$) was added to the solution to precipitate a yellow compound. After the mixture cooled to room temperature, the suspension was filtered, washed with ethanol (Scharlau, extra pure) and diethyl ether (Sigma–Aldrich, 99.9% spectrophotometric grade, inhibitor free), and dried under vacuum. The resulting complexes were used without any further purification. To obtain the cobalt(III) complex, the cobalt(II) complex was dissolved in acetonitrile, (Sigma–Aldrich, anhydrous 99.8%), and a slight excess of $NOBF_4$ (Sigma–Aldrich, 95%) was added. After removing the ACN by rotary evaporation, a large excess of NH_4PF_6 was added to the solution, and the desired compound was precipitated by adding diethyl ether. The solid was filtered, dried under vacuum, and used without further purification. The cobalt-based electrolytes consisted of 0.22 M $Co(L)_3(PF_6)_2$, 0.033 M $Co(L)_3(PF_6)_3$, 0.1 M $LiClO_4$ (Sigma–Aldrich, 99.9%) and 0.2 M 4-*tert*-butylpyridine (Sigma–Aldrich, 96%) in ACN, where L describes the different bidentate ligands. The I_3^-/I^- electrolyte was obtained from Solaronix (Iodolyte AN-50).

UV–visible steady-state absorption and fluorescence spectra were measured with JASCO V-670 and FluoroMax-4 (Jobin-Yvone) spectrophotometers, respectively.

2.1. Transient Absorption. The femtosecond transient UV–visible experiments were performed using the same setup described elsewhere.³⁵ Basically, it comprises a Ti/sapphire oscillator (TISSA 50, CDP Systems) pumped by a 5 W diode laser (Verdi 5, Coherent). The seed pulse (30 fs, 450 mW at 86 MHz) centered at 800 nm wavelength is directed to an

amplifier (Legend-USP, Coherent). The amplified fundamental beam (50 fs, 1 W at 1 kHz) is directed through an optical parametric amplifier for wavelength conversion (CDP Systems). The pump pulse intensity is kept constant at $125 \mu J / (\text{pulse} \cdot \text{cm}^2)$, and the average intensity is 4.1×10^{17} photons/ $(\text{cm}^2 \cdot \text{s})$. The excitation wavelength was 640 nm.

2.2. Flash Photolysis. The UV–visible and NIR nano-second to second flash photolysis setup consists of a LKS.60 laser flash photolysis spectrometer (Applied Photophysics), a Vibrant (HE) 355 II laser (Opotek) as a pump pulse source (5 ns time duration), and a 150 W xenon arc lamp as a probe. The signal from Optical parametric oscillator (355 nm pumped by Q-switched Nd/YAG laser, Brilliant, Quantel) at 640 nm was used for the sample excitation. The probing light transmitted through the sample was dispersed by a monochromator and detected by a UV–visible or NIR photomultiplier (thermo-electric cooled H10330–75 NIR-PMT module) coupled to a digital oscilloscope (Agilent Infiniium DS08064A, 600 MHz, 4 GSa/s). The pump energy pulse (5 mJ/pulse) was attenuated by a half-waveplate and a polarizer pair. The pump pulse energy density and pulse power density was $40\text{--}80 \mu J / \text{cm}^2$ and $0.4\text{--}0.8 \text{ mW} / \text{cm}^2$, respectively. All the experiments were done at 298 K. To simulate working conditions, a white LED (MWW HL3, Thorlabs) was used to achieve constant illumination of the solar cell ($100 \text{ mW} / \text{cm}^2$).

3. RESULTS AND DISCUSSION

3.1. Steady-State Absorption and Emission Spectroscopy. Figure 1 shows the normalized steady-state UV–visible absorption (solid line) and emission spectra (dashed line) of complete solar cells sensitized with SQ 8 (A) and SQ 12 (B), and containing the I_3^-/I^- redox pair. Similar spectra were obtained for the cells containing the Co-based electrolytes. Sharp absorption peaks centered at 648 and 663 nm are observed for the cells containing SQ 8 and SQ 12, respectively. The observed redshift ($15 \text{ nm} / 350 \text{ cm}^{-1}$) of the absorption maximum in SQ 12 is a consequence of the extension of π conjugation in the SQ backbone due to the insertion of the quinoline donor group (Chart 1). In addition to that, a blueshifted absorption shoulder is observed in both SQs, which was assigned to a high-energy vibronic transition.²³ The shape of these absorption spectra is very similar to those in solution (Figure S1, Supporting Information), but the wavelength of the maximum absorption is redshifted ($5 \text{ nm} / 161 \text{ cm}^{-1}$ and $7 \text{ nm} / 121 \text{ cm}^{-1}$ for SQ 8 and SQ 12, respectively). The latter has previously been explained in terms of the different environment of the SQ molecules at the surface of the TiO_2 nanoparticles.²³

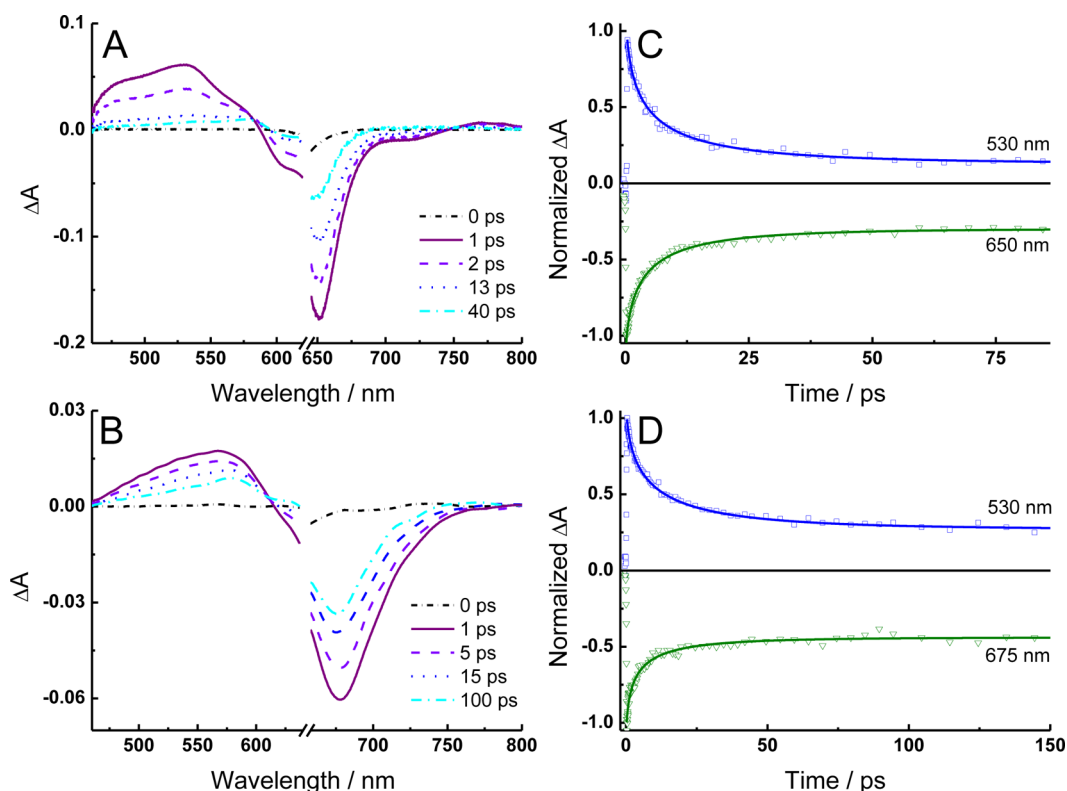


Figure 2. (A, B) Femtosecond transient absorption spectra (in terms of change in absorbance, ΔA) of a complete cell prepared with TiO_2 nanoparticles, containing the I^-/I_3^- electrolyte and sensitized with SQ 8 (A) and SQ 12 (B) at five pump–probe time delays. (C, D) Normalized decays of the transient signals (ΔA) at 530 and 650/675 nm of complete cells prepared with TiO_2 nanoparticles, containing the I_3^-/I^- electrolyte and sensitized with SQ 8 (C) and SQ 12 (D). The solid lines are from the best stretched exponential fits of the experimental data. The excitation wavelength was 640 nm.

The similar shape of the absorption spectra of the SQs in the complete cells and in solution points out the absence of aggregates in the former case. Since it is well known that SQs have high tendency to form aggregates, we have used a deaggregating agent, CDCA, which is coadsorbed together with the SQs onto the surface of the TiO_2 nanoparticles.²³ Figure 1 also shows the normalized emission spectra of the complete solar cells sensitized with SQ 8 (A) and SQ 12 (B) and containing the I_3^-/I^- redox pair. A redshift of the emission maxima is observed compared to those in solution, from 653 to 671 and from 703 to 713 nm for SQ 8 and SQ 12, respectively (Figure S1, Supporting Information). This is again a consequence of the different environment around the SQs between the two samples. The small Stokes shift of the emission (528 and 1050 cm^{-1} for SQ 8 and SQ 12, respectively) is very characteristic in the SQ molecules, indicating a comparable molecular configuration of the dye in the ground and excited states. The optical band gap for these SQs, E_g , has been calculated at the wavelength of the crossing point between normalized absorption and emission spectra (659 and 691 nm for SQ 8 and SQ 12, respectively).

3.2. Femtosecond Transient Absorption Studies. We used femtosecond transient absorption spectroscopy to study the electron injection dynamics in a set of solar cells containing the different studied electrolytes to probe their influence on the electron transfer process. The excitation wavelength was fixed at 640 nm, close to the maximum absorbance ($\lambda_{\text{max}} = 648$ and 663 nm for SQ 8 and SQ 12, respectively), to avoid interferences of the pump beam when probing at the maximum of the absorption peak. Low excitation fluence (125 $\mu\text{J}/$

(pulse· cm^2)) was used to minimize the concentration dependence of the deactivation processes, since a small fraction of the dyes will be excited with this energy as it happens in a cell under operating conditions. We have previously reported on concentration-dependence experiments on similar SQs in complete solar cells, and we found that, below $\sim 100\text{--}150 \mu\text{J}/(\text{pulse}\cdot\text{cm}^2)$, the concentration-dependence processes, that is, singlet–singlet annihilation, are not relevant to the photobehavior of the cell.³⁶

First, we describe the photodynamical behavior of complete solar cells containing I_3^-/I^- electrolyte and compare it later with that found in cells with the Co-based electrolytes. Figure 2A,B presents the transient absorption spectra at five pump–probe delay times for cells sensitized with SQ 8 and SQ 12, respectively. The transient spectra at 1 ps, exhibit a strong positive signal at the 450–575 nm region for both SQs and a very weak one at 770 nm found only for SQ 8. Similar signals in comparable spectra of other SQs have been previously attributed to the singlet excited state (S_1) of the SQ monomers.^{20,37} In addition to that, strong negative signals centered at 650/712 and 680 nm are observed for SQ 8 and SQ 12, respectively. We assign the weak band at 712 nm in SQ 8 to a contribution from stimulated emission. Although the maximum of the emission spectra is at 675 nm, an additional shoulder (not the maximum) was also observed in this spectral region (see Figure S1, Supporting Information). The other two strong negative signals are assigned to the bleach of the absorption peaks due to the strong depopulation of the ground state after excitation. It is worth remarking the redshift and the broader shape of the bleaching signal for SQ 12 with respect to

that of SQ 8, which agrees with that behavior observed in the steady-state absorption spectra. The evolution of the transient spectra at longer delay times provides information on the deactivation pathways of the singlet excited state. The most notable changes in these spectra are a redshift of the positive signals, from 530 nm (SQ 8) or 566 nm (SQ 12) to 575 nm (in both SQs) as well as the different shape of these transient bands, which are strongly asymmetric, with almost no absorption below 500 nm. This transient feature has previously been assigned to the signature of the radical cation of the SQs, $\text{SQ}^{\bullet+}$.^{19,22–24} This reflects the electron transfer from the excited SQ to the TiO_2 NP. Parallel to these changes, we also observe a decrease in the bleaching signal in both SQs and a rise of a weak positive band around 725 nm for the SQ 8 cell, being this latter signal attributed to $\text{SQ}^{\bullet+}$. It is worth noting that the transient absorption signal of the radical cation of the SQs must also extend to the 575–700 nm region, since the cation absorbs in the shorter (<575 nm) and longer wavelengths (>700 nm). However, this signal is “masked” due to its overlap with the negative ground-state bleach. The latter is confirmed by the observation of an isosbestic point around 590 nm, and the increase in the transient signal within the first few picoseconds at the red side of this region (formation of the radical cation). Thus, the recovery of the negative signal with time is due to its overlap with the positive transient signal of the radical cation.²³

We also carried out femtosecond experiments in complete cells containing Co-based electrolytes. Figures S2 and S3 in the Supporting Information show the transient absorption spectra at five delay times for each of the pump–probed cells containing each of the three Co-based electrolytes. The spectral behavior in both SQs is comparable to the one observed in the cells containing the I_3^-/I^- electrolyte. This result suggests that, in complete cells sensitized with SQ 8 or SQ 12, using Co-based electrolytes, the transient species involved in the femto-to-picosecond regime are not different when using the I_3^-/I^- electrolyte.

To quantify the dynamics of related processes in the complete cells, we analyzed the decays at two representative wavelengths. We probed the signals at 530 nm, assigned to the SQ singlet first excited-state absorption, and at the maximum of the bleach recovery, 650 and 675 nm for SQ 8 and SQ 12 cells, respectively (Figure 2C,D). At both wavelengths and up to 2 ns, the transient signals do not decay to zero, reaching a plateau with a constant value. This long signal is due to the $\text{SQ}^{\bullet+}$ present at these wavelengths. The decays were fit with a stretched exponential function (eq 1). The exponential distribution of TiO_2 density of states together with the energy distribution of the excited SQs are responsible for the stretched exponential dynamics of the electron injection process.³⁸

$$f(x) = A \exp[(-t/\tau)^\beta] \quad (1)$$

In eq 1, τ is the characteristic mean time of the signal decays, and β is the heterogeneity (dispersion) of the sample describing a Gaussian distribution of the energy states in the TiO_2 and the SQs.^{39,40} Moreover, to compare the τ values from the fits with different β parameters, it is necessary to define a weighted average effective lifetime, τ_{obs} , by means of eqs 2 and 3, where u is a variable of integration:⁴¹

$$\tau_{\text{obs}} = \frac{\tau}{\beta} \Gamma\left(\frac{1}{\beta}\right) \quad (2)$$

$$\Gamma\left(\frac{1}{\beta}\right) = \int_0^\infty u^{\frac{1}{\beta}-1} e^{-u} du \quad (3)$$

From the fits, we have obtained weighted average effective lifetimes of 7.2 and 6.2 ps for SQ 8 at 530 and 650 nm and 9.8 and 7.8 ps for SQ 12 at 530 and 675 nm, respectively. The small difference between the values at the two wavelengths for each SQ reveals that the recovery of the negative signal (formation of the radical cation) is associated to the decay of the singlet excited state. Figure 3 shows the normalized decays

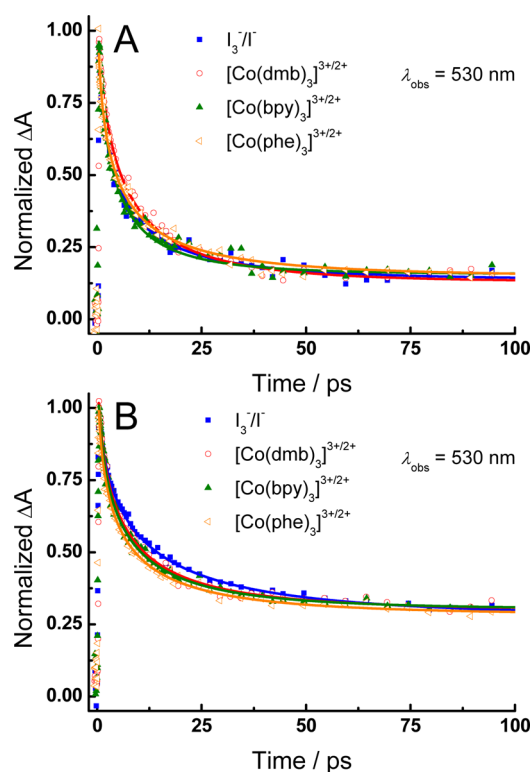


Figure 3. Normalized decays of the femtosecond transient signals (in terms of change in absorbance, ΔA) at 530 nm of complete cells prepared with TiO_2 nanoparticles, sensitized with SQ 8 (A) and SQ 12 (B) and containing I_3^-/I^- (full squares), $[\text{Co}(\text{dmb})_3]^{3+/2+}$ (circles), $[\text{Co}(\text{bpy})_3]^{3+/2+}$ (full triangles), and $[\text{Co}(\text{phe})_3]^{3+/2+}$ (empty triangles) electrolytes. Solid lines are from the best stretched exponential fits of the experimental data. The excitation wavelength was 640 nm.

of the transient absorption signals at 530 nm for complete cells sensitized with SQ 8 (A) and SQ 12 (B) and containing I_3^-/I^- or one of the Co-based electrolytes. For both SQs, the similar values of the singlet weighted average effective lifetime (Table 1) reflect that the dynamics of the electron injection process is independent of the type of the used electrolyte.

With the aim of determining the electron injection rate constant, k_{ei} , and the injection efficiency, φ_{ei} , it is necessary to calculate the lifetime of the singlet excited state of the SQs in comparable experimental conditions (adsorbed on the surface of the nanoparticles) but in the absence of the injection process. We prepared devices with the same structure, but instead of using TiO_2 nanoparticles, we used Al_2O_3 nanoparticles, which possess a ~ 4 eV less negative conduction band potential edge than that of TiO_2 but with the same binding properties.⁴² In that manner, we are preventing the electron injection, since the LUMO orbital of the SQ dyes is much lower in energy than the conduction band potential of the

Table 1. Values of the SQs S_1 Lifetimes, τ_{obs} , Derived from a Stretched Exponential Fit of the Decay of the Femtosecond Transient Absorption Signals (ΔA) at 530 nm of Complete Cells Prepared with TiO_2 and Al_2O_3 Nanoparticles, Sensitized with SQ 8 or SQ 12, and Containing Different Electrolytes^a

	electrolyte	τ_{obs} (TiO_2)/ ps	τ_{obs} (Al_2O_3)/ ps	$10^{-10} k_{\text{ei}}$ (TiO_2)/ s^{-1}	φ_{ei}	$-\Delta G^0_{\text{ei}}$ / eV
SQ 8	I_3^-/I^-	7.2	144	13.2	0.95	0.75
	$[\text{Co}(\text{dmb})_3]^{3+/2+}$	7.9		12.0	0.95	
	$[\text{Co}(\text{bpy})_3]^{3+/2+}$	5.7		16.8	0.96	
	$[\text{Co}(\text{phe})_3]^{3+/2+}$	6.5		14.7	0.95	
SQ 12	I_3^-/I^-	9.8	63	6.9	0.81	0.76
	$[\text{Co}(\text{dmb})_3]^{3+/2+}$	8.3		10.5	0.87	
	$[\text{Co}(\text{bpy})_3]^{3+/2+}$	8.3		10.5	0.87	
	$[\text{Co}(\text{phe})_3]^{3+/2+}$	8.2		10.6	0.87	

^aValues of the electron injection rate constants (k_{ei}), electron injection efficiencies (φ_{ei}), and driving forces ($-\Delta G^0_{\text{ei}}$) for the electron injection reaction.

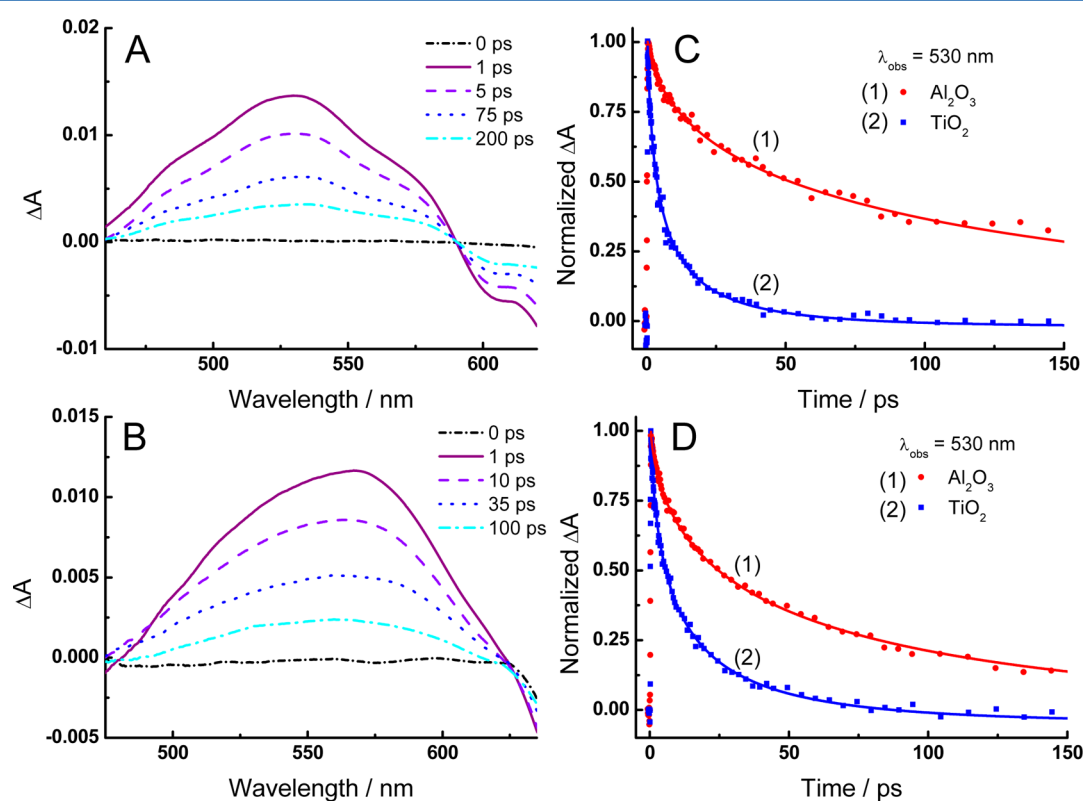


Figure 4. (A, B) Femtosecond transient absorption spectra (in terms of change in absorbance, ΔA) of a complete cell prepared with Al_2O_3 nanoparticles, containing the I_3^-/I^- electrolyte and sensitized with SQ 8 (A) and SQ 12 (B) at different pump–probe time delays. (C, D) Normalized decays of the transient signals (ΔA) at 530 nm of complete cells prepared with Al_2O_3 nanoparticles (red circles) or with TiO_2 nanoparticles (blue squares), sensitized with SQ 8 (C) and SQ 12 (D) and containing the I_3^-/I^- electrolyte. The solid lines are from the best stretched exponential fits of the experimental data. The excitation wavelength was 640 nm.

Al_2O_3 nanoparticles. Therefore, the singlet lifetime measured in these samples can be utilized to calculate the k_{ei} and φ_{ei} . Figure 4A,B illustrates the transient absorption spectra of complete cells prepared with Al_2O_3 nanoparticles containing the I_3^-/I^- electrolyte and sensitized with SQ 8 and SQ 12, respectively. The transient absorption spectra at 1 ps time delay exhibit strong positive bands centered at 530 and 570 nm for SQ 8 and SQ 12, respectively. These transient features are similar to other SQs and were previously assigned to the S_1 state of the SQs.^{23,24} The evolution of these spectra at longer time delays showed no changes in the shape, which confirms the absence of the transient feature of the $\text{SQ}^{\bullet+}$ species and therefore the electron injection from SQ to Al_2O_3 nanoparticles. Figure 4C,D displays the transient absorption decays at 530 nm for SQ 8 and

SQ 12, respectively. For comparison, decays at the same wavelength for the samples prepared with TiO_2 nanoparticles are also shown for comparison. Clearly, the transient decays for the samples with Al_2O_3 are much longer than those with TiO_2 , which indicates additional deactivation processes using the TiO_2 nanoparticles (electron injection). We have also used stretched exponential functions to fit the transient decays of the samples with Al_2O_3 , resulting in lifetimes, τ_{obs} , of 144 and 63 ps for SQ 8 and SQ 12, respectively (Table 1).

The electron injection rate constant can be obtained by using the previously calculated lifetimes for the singlet excited state by eq 4 (Table 1):

$$k_{\text{ei}} = \frac{1}{\tau_{\text{TiO}_2}} - \frac{1}{\tau_{\text{Al}_2\text{O}_3}} \quad (4)$$

where τ_{TiO_2} and $\tau_{\text{Al}_2\text{O}_3}$ are the effective lifetimes (τ_{obs}) for the cells with TiO_2 and Al_2O_3 nanoparticles, respectively. We obtained k_{ei} values of 13.2×10^{10} and $6.9 \times 10^{10} \text{ s}^{-1}$ for the cells containing the I_3^-/I^- electrolyte and sensitized with SQ 8 and SQ 12, respectively. These values are in good agreement with those obtained for similar asymmetric SQs compared to the smaller values for the symmetric ones.²⁴ This behavior has been explained by the unidirectional flow of electrons to the TiO_2 nanoparticles in asymmetric SQs. The driving force of the electron injection reaction, ΔG^0_{ei} , is also shown in Table 1 (-0.75 and -0.76 eV for SQ 8 and SQ 12, respectively).⁴³ The similar ΔG^0_{ei} values for both SQs do not explain the difference in the k_{ei} values. Therefore, the electronic coupling, V , that is, the interaction between the LUMO of the SQs and the conduction band of the TiO_2 nanoparticles, is assumed to be an important factor influencing the injection (Marcus theory for electron transfer processes). Previous computational studies on these dyes have shown that the electron density in the LUMO at the side of the carboxylic acid is much lower in SQ 12 compared to that in SQ 8.³² Moreover, the highest occupied molecular orbital (HOMO) is mainly located at the squaric core in SQ 8, whereas there is high electron density at the quinoline and indole donor moieties in SQ 12. This produces a weaker unidirectional flow of electrons in SQ 12 than in SQ 8. All the previous theoretical results suggest a poorer electronic coupling in the SQ 12/ TiO_2 system, which means a smaller value for the rate constant of the electron injection process and therefore a much lower relative efficiency.

We also calculated the k_{ei} values for the cells containing the Co-based electrolytes and the obtained values are as follows: 12.0×10^{10} , 16.8×10^{10} , and $14.7 \times 10^{10} \text{ s}^{-1}$ for SQ 8 with $[\text{Co}(\text{dmb})_3]^{3+/2+}$, $[\text{Co}(\text{bpy})_3]^{3+/2+}$, and $[\text{Co}(\text{phe})_3]^{3+/2+}$, respectively, and $10.5 \times 10^{10} \text{ s}^{-1}$ for SQ 12 with the three electrolytes (Table 1). Comparing the k_{ei} values among the Co-based electrolytes, we observed small variations for SQ 8 and no changes at all for SQ 12. This result indicates that the different ligands in the Co complexes do not modify the injection dynamics. We can also compare the k_{ei} values for the cells containing the I_3^-/I^- and the Co-based electrolytes. Using SQ 8, the k_{ei} value with I_3^-/I^- falls between those with the Co-based electrolytes, while for SQ 12 the k_{ei} value is slightly lower. On the basis of these observations, we conclude that the electron injection in the complete cells sensitized with SQ 8 and SQ 12 is not affected by the type of the used electrolyte.

Finally, the electron injection efficiency for each cell can be calculated by using eq 5 (Table 1).

$$\varphi_{\text{ei}} = \frac{k_{\text{ei}}}{k_{\text{ei}} + \frac{1}{\tau_{\text{Al}_2\text{O}_3}}} \quad (5)$$

The obtained values for φ_{ei} are much larger in the cells sensitized with SQ 8 than with SQ 12. This is a consequence of the larger values of k_{ei} in SQ 8. Note also the longer lifetime of the singlet excited state in the samples without injection, with Al_2O_3 nanoparticles (144 vs 63 ps). This is an interesting result, since the efficiency of the electron injection depends on the competition between the electron transfer process and other deactivation processes.

Now, we compare the electron injection efficiencies with the obtained values for the short circuit current density, J_{sc} . First,

the higher values of φ_{ei} in SQ 8 with respect to SQ 12 relate well with the larger J_{sc} value for SQ 8 (7.22 vs 6.61 mA/cm^2 with the I_3^-/I^- electrolyte). Although the electron injection is not the only reaction controlling the J_{sc} , the good relationship can partially explain the larger J_{sc} in SQ 8. Second, the similar values of φ_{ei} between the I_3^-/I^- and the Co-based electrolytes are not in agreement with the much lower value of J_{sc} in the solar cells containing the Co-based electrolytes (1.99 vs 7.22 mA/cm^2 for SQ 8 with $[\text{Co}(\text{dmb})_3]^{3+/2+}$ or I_3^-/I^- redox electrolyte). This indicates that the key factor in the low efficiency of the SQ-based solar cells containing the Co-based electrolytes is not the electron injection process but the regeneration or recombination processes (vide infra).

To summarize this section, we have obtained the k_{ei} and φ_{ei} values for the complete solar cells sensitized with SQ 8 or SQ 12 and containing either the Co-based or the I_3^-/I^- electrolytes. Both parameters are much larger for SQ 8 compared to those for SQ 12 in all the used electrolytes, which is explained by its larger electronic coupling. Therefore, this result can account for the larger J_{sc} in SQ 8. However, the most relevant result is the similarity of the values for k_{ei} and φ_{ei} in the same SQ among the different electrolytes (I_3^-/I^- or Co-based electrolytes), which reflects the limited influence of the electrolyte on the electron injection. Thus, the large variation of J_{sc} found for the different electrolytes does not result from the injection reaction, and therefore, it is necessary to study the electron regeneration and recombination processes.

3.3. Nanosecond Transient Absorption Studies. Flash photolysis experiments were carried out in order to evaluate the photodynamics of the regeneration and recombination processes. These experiments were performed under constant illumination with a white LED (100 mW/cm^2) to simulate working conditions at open circuit voltage. As a result, the equilibrium among the different electron transfer processes is reached in the device, and therefore, the concentration of electrons in the TiO_2 nanoparticles is constant.^{44,45} Thus, with the small perturbation of the system caused by the pumping beam (50 $\mu\text{J}/(\text{cm}^2 \cdot \text{pulse})$), it is possible to obtain the rate constants of the different reactions in the operating device.

Figure 5 shows the transient absorption spectra in the visible–NIR region for a complete solar cell sensitized with SQ 8 (A) and SQ 12 (B) containing the I_3^-/I^- redox pair. The same shape in the transient spectra was measured in cells containing each of the Co-based electrolytes or with the inert electrolyte (no redox pair being present), which indicates that the nature of the transient species is independent of the used electrolyte. In the visible region, we observed the same transient features as in the femtosecond transient absorption spectra at long time delays ($\sim 100 \text{ ps}$): two positive signals around 530–580 and 720–750 nm, with a bleach band at around 650–670 nm, matching the steady-state absorption spectrum. The positive signals are attributed to the radical cation of the SQs, $\text{SQ}^{\bullet+}$. We did not detect changes in the shape of the spectra with the different delay times, indicating that $\text{SQ}^{\bullet+}$ deactivates directly to the ground state. In the NIR region, we found a broad positive signal throughout the spectrum up to 1550 nm. The behavior of this signal is dependent on the observed wavelength. From 950 to 1300 nm, the signal decays with a similar time constant as in the visible region (7 and 76 μs with I_3^-/I^- for SQ 8 and SQ 12, respectively), which is assigned to the radical cation of the SQs. On the other hand, throughout the NIR spectrum, there is a broad band with no clear maximum, which decays slower than the transient feature

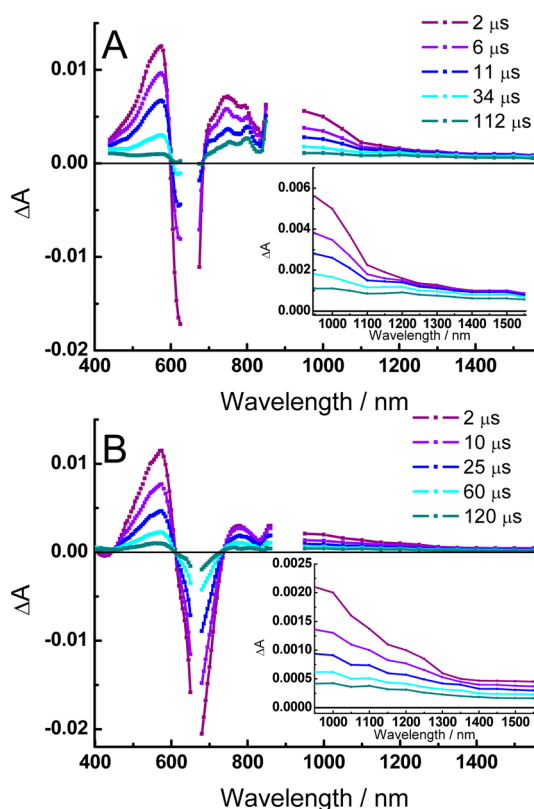


Figure 5. Nanosecond transient absorption spectra of complete cells sensitized with SQ 8 (A) and SQ 12 (B) and containing the I_3^-/I^- electrolyte at five time delays. The excitation wavelengths were 650 and 675 nm, for SQ 8 and SQ 12, respectively.

assigned to SQ^{*+} . This broad band has been previously attributed to the absorption spectrum of electrons in d–d transitions of Ti^{3+} species.^{46,47} The time evolution of this signal allows us to investigate the dynamics of the electron recombination process via dye or electrolyte.

In the cells containing solely the inert electrolyte, without the redox pair, the only electron recombination reaction is via dye. The transient absorption decays at 570 (dye cation signal) and 1550 nm (electron signal) were measured under constant illumination with a white LED (1 sun) for those samples (Figure S4, Supporting Information). As expected, both decays are virtually coincident, demonstrating that all injected electrons recombine with the dye cation. The obtained lifetimes are 175 and 170 μs at 570 and 1550 nm for SQ 8 and 256 and 250 μs at the same wavelengths for SQ 12 (Table 2). The rate constants for this recombination process ($k_{rec/dye}$, Scheme 1), calculated as the inverse of the lifetimes, are 5.7 and $3.9 \times 10^3 s^{-1}$ for SQ 8 and SQ 12, respectively. The observed difference

in the recombination rate constants between the two SQs can be accounted for by the greater driving force, ΔG_{rec} for SQ 8 compared to that for SQ 12 (-1.13 vs -1.03 eV), obtained as the difference between the oxidation potential of the dyes and the energy of the conduction band of the TiO_2 nanoparticles (-4.0 eV).

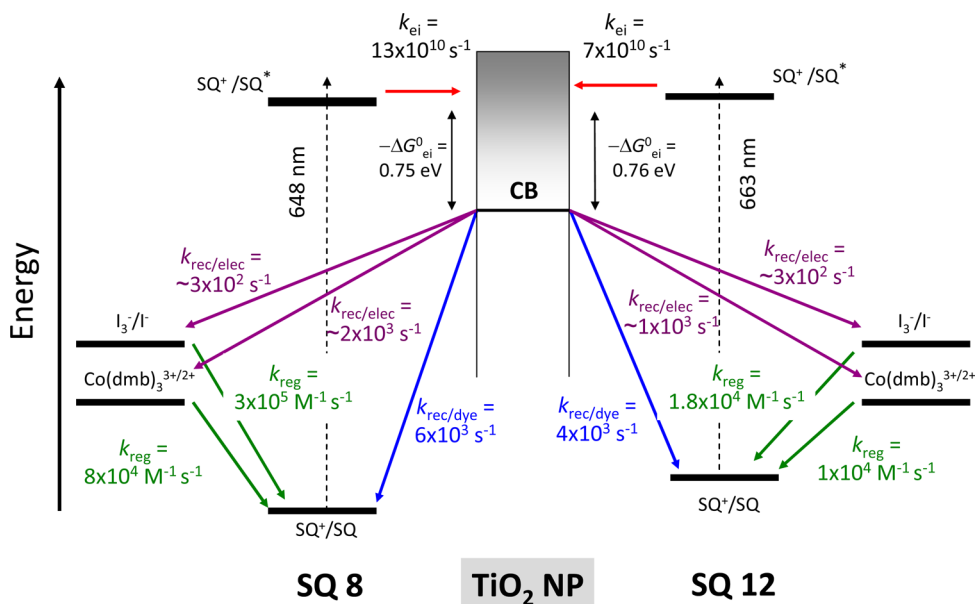
In the complete solar cells, upon addition of the redox electrolytes to the system and with sufficiently fast regeneration process, the radical cation of the SQs is reduced by the redox pair, preventing the recombination of the electrons via dye cation. Therefore, the only recombination pathway of the electrons should be with the oxidized species of the redox pair (recombination via electrolyte, $k_{rec/elect}$, Scheme 1). Figure 6 shows the decay of the transient signal at 1550 nm (transient signal of the electrons) for complete cells sensitized with SQ 8 (A) and SQ 12 (B) and containing the I_3^-/I^- or the $[Co(dmb)_3]^{3+/2+}$ redox pair. These decays were fitted using stretched exponential functions, and the obtained lifetimes are exhibited in Table 2. The most remarkable result is the different lifetimes, 3 versus ~ 0.5 –1 ms, obtained for the cells with the I_3^-/I^- or the different $[Co(L)_3]^{3+/2+}$ electrolytes in both SQs, respectively.⁴⁸ This clearly points out a different kinetics for the recombination of the electrons in the TiO_2 nanoparticles depending on the used electrolytes. Thus, the electron lifetime is about 6 and 3 times longer with the I_3^-/I^- compared to the different $[Co(L)_3]^{3+/2+}$ electrolytes in cells sensitized with SQ 8 or SQ 12, respectively. This result is in line with the well-known fact that the one-electron redox mediators, as the Co-based electrolytes, have faster recombination dynamics with the photogenerated electrons than the two-electron redox couple, I_3^-/I^- .^{27,34,49,50} It is worth remarking the short electron lifetimes in SQ 8 with $[Co(phen)_3]^{3+/2+}$ and in SQ 12 with $[Co(bpy)_3]^{3+/2+}$ and $[Co(phen)_3]^{3+/2+}$, $\sim 250 \mu s$, which are similar to those obtained for the samples containing solely the inert electrolyte, without the redox pair. Thus, in these samples, the electron recombination proceeds via dye cation due to the poor regeneration reaction (vide infra).

The common strategy to suppress the fast recombination with the two-electron mediators is the use of bulky groups attached to the organic sensitizers.²⁷ However, in light of our results, we can conclude that the steric hindrance in our SQ 8 and SQ 12 is not sufficient to prevent the approach of the Co^{3+} species to the surface of the TiO_2 nanoparticle. Moreover, the electron lifetimes are always longer for SQ 12 compared to those for SQ 8 when using the same Co-based electrolyte ($\sim 1000 \mu s$ vs $\sim 500 \mu s$), showing that the steric hindrance is more intense in SQ 12 (as it is expected due to the bulkier substituents, quinoline group, and the octyl alkyl chain). Finally, we can compare the obtained electron lifetimes in our system, ~ 0.5 –1 ms, with others previously published for similar Co-based electrolytes. Thus, the electron lifetimes are around 1

Table 2. Values of Lifetimes, τ_{obs} , Derived from a Stretched Exponential Fit of the Decay of the Flash Photolysis Signals at 570 and 1550 nm of Complete Cells Prepared with TiO_2 Nanoparticles, Sensitized with SQ 8 or SQ 12, with and without Electrolyte

		$\tau_{\text{obs}}/\mu\text{s}$				
		no electrolyte	electrolyte			
	$\lambda_{\text{obs}}/\text{nm}$		I_3^-/I^-	$[\text{Co}(\text{dmb})_3]^{3+/2+}$	$[\text{Co}(\text{bpy})_3]^{3+/2+}$	$[\text{Co}(\text{phe})_3]^{3+/2+}$
SQ 8	570	175	7	43	81	173
	1550	170	3100	500	600	250
SQ 12	570	256	76	141	238	244
	1550	250	3300	1100	300	260

Scheme 1. Energy Level Diagram (Not in Scale) Giving the Values of the Rate Constants Involved in the SQ 8 and SQ 12 Based DSSCs Containing I_3^-/I^- or $[Co(dmb)_3]^{3+/2+}$ Redox Electrolyte^a



^aThe rate constants k_{ei} , $k_{rec/dye}$, $k_{rec/elec}$ and k_{reg} stand for electron injection, recombination via dye, recombination via electrolyte, and dye regeneration, respectively.

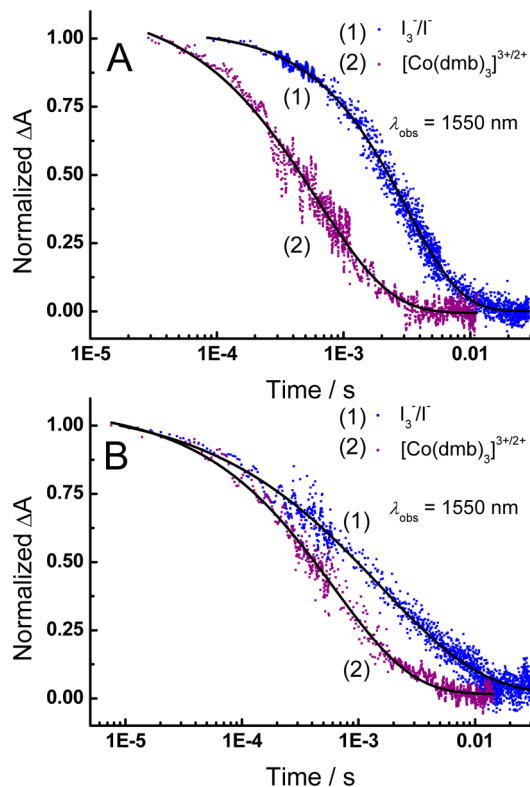


Figure 6. Normalized decays of the flash photolysis signals (in terms of change in absorbance, ΔA) at 1550 nm of complete cells sensitized with SQ 8 (A) or SQ 12 (B) and containing the I_3^-/I^- (blue line) or the $[Co(dmb)_3]^{3+/2+}$ electrolyte (purple line). The excitation wavelengths were 650 and 675 nm, for SQ 8 and SQ 12, respectively.

ms for a carbazole-based dye,⁵¹ 2–3 ms for the champion porphyrin,²⁸ and 3–10 ms for triphenylamine-based dyes.⁸ The lifetime of the injected electrons in the TiO₂ nanoparticles is

short in our devices sensitized with the different SQs due to the recombination of the electrons via the electrolyte, and as a consequence, the extracted photocurrent is expected to be lower than that of devices with other types of sensitizers. We suggest that, to elongate the lifetime of the electrons in the TiO₂ nanoparticles in SQ-based solar cells containing the Co-based electrolytes, it is necessary to introduce a larger steric hindrance in the SQ backbone, which hampers the recombination of the electrons with the electrolytes.

In the complete solar cells containing the redox electrolyte, the dye regeneration process was followed by measuring the change in the transient absorption signal at 570 nm, where the maximum of the transient signal of SQ^{+*} appears. Figure 7 shows the decays of the signals at 570 nm for the complete cells sensitized with SQ 8 (A) and SQ 12 (B) and containing the I_3^-/I^- or the $[Co(dmb)_3]^{3+/2+}$ redox electrolyte. The fit of the signals to stretched exponential functions (eq 1) gives an average effective lifetimes (τ_{obs}) of 7 and 43 μs for SQ 8 and 76 and 141 μs for SQ 12 with the I_3^-/I^- or the $[Co(dmb)_3]^{3+/2+}$ electrolytes, respectively (Table 2). In both cases, the dye regeneration process is faster in the cells with the I_3^-/I^- than with the $[Co(dmb)_3]^{3+/2+}$ redox electrolyte and for cells sensitized with SQ 8 compared to those with SQ 12. Table 2 also gives the τ_{obs} for cells containing the other two Co-based electrolytes, 81 and 179 μs (SQ 8) and 238 and 244 μs (SQ 12) with the $[Co(bpy)_3]^{3+/2+}$ and the $[Co(phen)_3]^{3+/2+}$ electrolytes, respectively. These regeneration lifetimes are clearly longer compared to the cells with the $[Co(dmb)_3]^{3+/2+}$ electrolyte (Figure S5, Supporting Information).

The regeneration rate constant, k_{reg} , can be obtained by using eq 6 and the previously calculated value for the recombination, k_{rec} :

$$k_{reg} = \frac{k_{obs} - k_{rec}}{[\text{electrolyte}]} \quad (6)$$

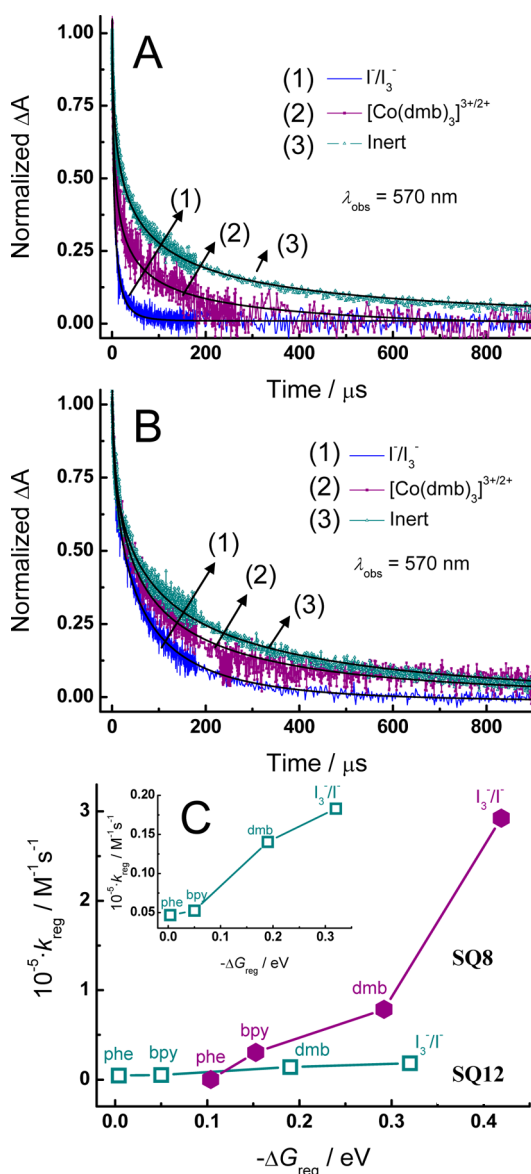


Figure 7. (A, B) Normalized decays of the flash photolysis signals (in terms of change in absorbance, ΔA) at 570 nm of complete cells sensitized with SQ 8 (A) and SQ 12 (B), containing the I_3^-/I^- (1), the $[\text{Co}(\text{dmb})_3]^{3+/2+}$ (2) electrolyte or without electrolyte (3). The solid lines are from the best stretched exponential fits of the experimental data. The excitation wavelengths were 650 and 675 nm, for SQ 8 and SQ 12, respectively. (C) Variation of k_{reg} with $-\Delta G_{\text{reg}}$ for SQ 8 and SQ 12 complete cells using different electrolytes. The inset of (C) is a zoom of k_{reg} with $-\Delta G_{\text{reg}}$ for SQ12-based cell.

where [electrolyte] refers to the concentration of the reduced species of the redox pair. Table 3 gives the obtained rate constants for the cells sensitized with SQ 8 or SQ 12 and containing the different redox electrolytes. With the aim of giving an insight into these values, the driving forces of the regeneration reactions were obtained by using eq 7 (Table 3):

$$-\Delta G_{\text{reg}} = E_{1/2}(\text{S}^+/\text{S}) - E_{1/2}(\text{electrolyte}) \quad (7)$$

where $E_{1/2}(\text{S}^+/\text{S})$ and $E_{1/2}(\text{electrolyte})$ are the redox potentials of the dye and the electrolyte, respectively. The standard potentials have been obtained by cyclic voltammetry (Figures S6 and S7, Supporting Information) giving values of 0.46, 0.60, 0.64, 0.70, and 0.60 V versus the normal hydrogen electrode

(NHE) for $[\text{Co}(\text{dmb})_3]^{3+/2+}$, $[\text{Co}(\text{bpy})_3]^{3+/2+}$, $[\text{Co}(\text{phe})_3]^{3+/2+}$, SQ 8, and SQ 12, respectively. The redox potentials of the electrolytes are derived from the Nernst equation, according to the relative concentrations of the oxidized and reduced species employed in the measured solar cell. Figure 7C plots the k_{reg} values versus $-\Delta G_{\text{reg}}$ for all the electrolytes. We find good correlation among the values of k_{reg} and $-\Delta G_{\text{reg}}$ for both SQs, including the I_3^-/I^- redox pair, which has a different electron transfer mechanism.

Finally, the regeneration efficiency can be calculated for each SQs and redox electrolyte using eq 8 (Table 3):

$$\varphi_{\text{reg}} = \frac{k_{\text{reg}}}{k_{\text{reg}} + k_{\text{rec}}} \quad (8)$$

The highest value ($\varphi_{\text{reg}} = 0.96$) is found for SQ 8 with I^-/I_3^- . Lower values, $\varphi_{\text{reg}} = 0.70$ – 0.75 , are calculated for SQ 8 with $[\text{Co}(\text{dmb})_3]^{3+/2+}$ and SQ 12 with I^-/I_3^- and, $\varphi_{\text{reg}} = 0.44$ – 0.54 , for SQ 8 with $[\text{Co}(\text{bpy})_3]^{3+/2+}$ and SQ 12 with $[\text{Co}(\text{dmb})_3]^{3+/2+}$. Finally, values of φ_{reg} close to zero were obtained for SQ 8 with $[\text{Co}(\text{phen})_3]^{3+/2+}$ and SQ 12 with $[\text{Co}(\text{bpy})_3]^{3+/2+}$ and $[\text{Co}(\text{phen})_3]^{3+/2+}$.

The φ_{reg} values in both SQs for cells containing the Co-based electrolytes are lower than those of the corresponding cells with the I_3^-/I^- redox pair. This behavior can be clearly explained by the different driving forces, $-\Delta G_{\text{reg}}$, among the different electrolytes. Thus, in these two SQs, the $-\Delta G_{\text{reg}}$ values below 0.30 eV are not providing a complete regeneration efficiency as it happens in carbazole-based dyes with ferrocene derivative electrolytes ($\varphi_{\text{reg}} = 0.99$ with $-\Delta G_{\text{reg}} \approx 0.20$ – 0.25 eV).⁵² However, when comparing with similar Co-based electrolytes in other dyes, the φ_{reg} values are intermediate. On one side, porphyrin-based cells containing the $[\text{Co}(\text{bpy})_3]^{3+/2+}$ complex as the redox electrolyte with $-\Delta G_{\text{reg}} \approx 0.28$ – 0.35 eV have been reported to generate record efficiencies, which assures a complete regeneration.²⁸ On the other hand, in triphenylamine-based cells, values of $\varphi_{\text{reg}} \approx 0.56$ – 0.70 were obtained for $-\Delta G_{\text{reg}}$ similar to those in our systems (0.26–0.39 eV), necessitating $-\Delta G_{\text{reg}} > 0.55$ eV to achieve an almost complete regeneration, $\varphi_{\text{reg}} > 0.95$.⁸ Thus, the regeneration efficiency is clearly dependent on the type of dye and not only on the $-\Delta G_{\text{reg}}$. The use of Co-based electrolytes in our SQ-based solar cells is detrimental to the overall efficiency, since the consequent reduction of the $-\Delta G_{\text{reg}}$ produces no complete regeneration efficiency. One possible strategy to increase the φ_{reg} could be to decrease the k_{rec} by fine-tuning of the molecular orbitals in the SQs (lower coupling with the TiO_2) or to insert long bridges between the SQs and the TiO_2 nanoparticle, but without affecting the electron injection process. Moreover, the φ_{reg} values are found much larger for SQ 8 than those for SQ 12 when comparing cells having the same electrolyte. This behavior can again be explained by greater $-\Delta G_{\text{reg}}$ for SQ 8 compared to that of SQ 12, which is a consequence of the more positive oxidation potential of SQ 8. Thus, contrary to the beneficial extension of the absorption spectrum to the red for SQ 12, due to its lower energy of the HOMO, this also produces a negative effect on the regeneration efficiency.

We have also measured the current–voltage (I – V) curves for each cell. We obtained different photoelectrochemical parameters: short circuit photocurrent density, J_{sc} , open circuit voltage, V_{oc} , and power conversion efficiency, η , (Table 3). First, the V_{oc} values for the cells containing the Co-based electrolytes are lower than expected (0.72 vs ~ 0.33 V for SQ 8

Table 3. Values of the Rate Constants, k_{reg} , Driving Forces, $-\Delta G_{\text{reg}}$, and Efficiencies, φ_{reg} , for the Regeneration Process, Obtained Using eqs 6–8, respectively, for Solar Cells Sensitized with SQ 8 and SQ 12 and with Different Electrolytes^a

dye	DSSC characteristic	electrolytes used			
		I_3^-/I^-	$[\text{Co}(\text{dmb})_3]^{3+/2+}$	$[\text{Co}(\text{bpy})_3]^{3+/2+}$	$[\text{Co}(\text{phe})_3]^{3+/2+}$
SQ 8	$10^{-3} \cdot k_{\text{reg}} / \text{M}^{-1} \text{s}^{-1}$	293	79.2	31.0	0.18
	$-\Delta G_{\text{reg}} / \text{eV}$	0.42	0.29	0.15	0.10
	φ_{reg}	0.96	0.75	0.54	0.01
	$\eta / \%$	3.28	0.26	0.18	0.08
	$J_{\text{sc}} / \text{mA} \cdot \text{cm}^{-2}$	7.22	1.99	1.45	0.84
	V_{oc} / V	0.72	0.32	0.34	0.32
	$10^{-3} \cdot k_{\text{reg}} / \text{M}^{-1} \text{s}^{-1}$	18.3	14.3	1.2	0.8
SQ 12	$-\Delta G_{\text{reg}} / \text{eV}$	0.32	0.19	0.05	0.01
	φ_{reg}	0.70	0.44	0.07	0.04
	$\eta / \%$	2.29	0.09	0.02	0.01
	$J_{\text{sc}} / \text{mA} \cdot \text{cm}^{-2}$	6.61	1.19	0.37	0.13
	V_{oc} / V	0.61	0.24	0.20	0.21

^aPhotoconversion efficiencies, η , short-circuit current densities, J_{sc} , and open circuit voltages, V_{oc} , were obtained from the current–voltage curves (I – V).

and 0.61 vs ~ 0.22 V for SQ 12 with the I_3^-/I^- or the Co-based electrolytes, respectively). Thus, the strategy of using redox pairs with more positive oxidation potential than that of the I_3^-/I^- couple is not working with these SQs. The V_{oc} value in a solar cell is strongly dependent on the electron concentration in the semiconductor, which is proportional to the rate constant of the recombination processes.⁵³ In these SQs, the rather poor regeneration efficiency with the Co-based electrolytes results in a significant recombination of the electrons with the dye cation, which explains the low V_{oc} values. Second, the J_{sc} values for each cell are compared to each other and with the regeneration efficiencies. For the cells containing the Co-based electrolytes, J_{sc} values are much lower than those obtained when using the I_3^-/I^- redox pair. For example, for the case of SQ 8, $J_{\text{sc}} = 7.22$ or 1.99 mA/cm^2 for I_3^-/I^- or $[\text{Co}(\text{dmb})_3]^{3+/2+}$, respectively. This result can be accounted for the faster recombination via electrolyte in the cells containing the Co-based electrolytes but also due to the slower regeneration process. Thus, there is a good correlation between the J_{sc} and the φ_{reg} for all the used electrolytes; the larger is the φ_{reg} value, the higher is the J_{sc} measured. To conclude this point, the regeneration efficiency and the J_{sc} value are directly related to the $-\Delta G_{\text{reg}}$. Thus, to obtain an efficient regeneration process with SQ 8 or SQ 12, it is necessary to use electrolytes with redox potentials generating a $-\Delta G_{\text{reg}}$ value larger than 0.4 eV.

Finally, we have also compared the rate constants and efficiencies obtained for SQ 8 and SQ 12 containing the I_3^-/I^- redox pair with those previously obtained for similar asymmetric or symmetric indole-based SQs.²⁴ The asymmetric indole-based squaraine, SQ 8, shows a k_{ei} very similar to that found for SQ 41 (another asymmetric dye), while it is much larger than those described for the symmetric ones. Thus, for the asymmetric squaraines SQ 8 and SQ 41, we have found $k_{\text{ei}} = 13.2 \times 10^{10}$ and $14 \times 10^{10} \text{ s}^{-1}$, respectively, whereas for the symmetric squaraines SQ 26 and SQ 4, these values are $k_{\text{ei}} = 3 \times 10^{10}$ and $8 \times 10^{10} \text{ s}^{-1}$, respectively. This result reflects the great importance of the unidirectional flow of electrons in the injection when using the asymmetric SQs. Regarding the regeneration process, k_{reg} is almost identical in the asymmetric SQs, $k_{\text{reg}} = 2.9 \times 10^5$ and $1.8 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$ for SQ 8 and SQ 41, respectively. To compare, for the symmetric SQ 26, $k_{\text{reg}} = 9.9 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$, which is considerably larger than those of the asymmetric ones. This is due to the presence of two

trifluoromethyl groups, $-\text{CF}_3$, which induce higher positive charge density on the SQ backbone, favoring the interaction between the $\text{SQ}^{\bullet+}$ and the I^- species. Like the asymmetric quinoline-based squaraine, SQ 12 presents $k_{\text{ei}} = 6.9 \times 10^{10} \text{ s}^{-1}$ similar to the values observed for the symmetric SQs. Therefore, in order to obtain an unidirectional flow of electrons, not only an asymmetric SQ is necessary, but also, high electron densities in the LUMO at the carboxylic group and the HOMO located along the molecule are key issues. Regarding the regeneration rate constant, k_{reg} , it is especially low for SQ 12, $1.8 \times 10^4 \text{ M}^{-1} \text{s}^{-1}$, which in this case, can be explained by its energetics and not due to structural requirements.

To summarize this nano- to millisecond part, we have shown that the molecular structure of the SQs largely affects the injection and regeneration dynamics. Thus, the proposed structure, which can give the higher photocurrent, would be an asymmetric SQ with electron density on the LUMO located at the carboxylic group and the HOMO mainly localized at the squaric core. We have found that the relatively low efficiency of our solar cells containing the Co-based electrolytes is due the faster recombination via the electrolyte and the slower regeneration process, with low values of the driving forces, $-\Delta G_{\text{reg}}$. In consequence, to obtain a complete regeneration process, it is necessary to have a $-\Delta G_{\text{reg}}$ value larger than 0.4 eV. Thus, the strategy of using redox pairs with more positive oxidation potential than that of the I_3^-/I^- couple is not working with these SQs.

4. CONCLUSIONS

We have fabricated a series of DSSCs with two types of SQs, indole and quinoline based, and two types of redox electrolytes, the commonly used I_3^-/I^- and three different Co-based complexes with different oxidation potentials, $[\text{Co}(\text{dimethylbipyridine})_3]^{3+/2+}$, $[\text{Co}(\text{bipyridine})_3]^{3+/2+}$, and $[\text{Co}(\text{phenanthroline})_3]^{3+/2+}$. The quinoline-based squaraine (SQ 12) is selected due to its absorption spectrum being shifted to the NIR region (up to $\sim 725 \text{ nm}$) compared to SQ 8 (up to $\sim 680 \text{ nm}$), which is a particularly interesting feature, since there are not many organic dyes capable of absorbing NIR photons. The three Co-based electrolytes possess oxidation potentials between 0.1 and 0.3 V more positive than that of the I_3^-/I^- pair, which should increase the open circuit voltage, V_{oc} .

of the cell and therefore the overall efficiency. However, the measured photocurrent was lower for SQ 12 and for the cells containing the Co-based redox electrolytes. To gain an insight into these results, the transient UV–visible–NIR absorption pump–probe techniques were utilized to get the rate constants and efficiencies of the different processes. Thus, the injection and regeneration efficiencies for SQ 8 are both larger than those for SQ 12, which is explained in terms of a larger electronic coupling, V , in the injection and the driving forces for the regeneration, $-\Delta G_{\text{reg}}$ in SQ 8 (Scheme 1). Thus, the insertion of the extended π -conjugated quinoline group decreases the electron density in the LUMO at the carboxylic acid, which results in a weaker unidirectional flow of electrons, since the HOMO is more spread along the molecule, and not mainly on the squaric core. Also, the oxidation potential of SQ 12 is less positive (vs NHE) than that of SQ 8, which provokes that the $-\Delta G_{\text{reg}}$ values are not large enough to accomplish the complete regeneration ($-\Delta G_{\text{reg}} = 0.32$ eV with the I_3^-/I^- pair). Finally, the calculated injection efficiency, ϕ_{ei} , is similar across cells with I_3^-/I^- or any of the Co-based redox pairs, which reflects the limited influence of the electrolyte on the electron injection ($\phi_{\text{ei}} = 0.95$ or 0.96 for SQ 8 with I_3^-/I^- or $[\text{Co}(\text{bpy})_3]^{3+/2+}$, respectively). However, there is a large difference in the regeneration efficiencies between both types of electrolytes, for example, in SQ 8, $\phi_{\text{reg}} = 0.96$ or 0.75 with I_3^-/I^- or $[\text{Co}(\text{dmb})_3]^{3+/2+}$, respectively. The lower photocurrent with the Co-based electrolytes accounts for the lower ϕ_{reg} values, resulting from its lower regeneration driving force, $-\Delta G_{\text{reg}}$. Importantly, in our SQ-based solar cells, to achieve a complete regeneration process and therefore a high value of photocurrent, $-\Delta G_{\text{reg}}$ must be greater than 0.4 eV, which does not favor the use of these Co-based electrolytes as beneficial to increase the overall efficiency. Another result of this work is that the electron recombination via electrolyte was dependent on the used electrolyte (Scheme 1), which indicates that these SQs are not bulky enough to avoid the interaction between the Co^{3+} species and the electron in the TiO_2 nanoparticles.

■ ASSOCIATED CONTENT

■ Supporting Information

Steady-state absorption and emission spectra of both SQs in an EtOH solution or in a complete solar cell; picosecond time-resolved transient absorption spectra and normalized decays of the transient signals at 530, 665, and 675 nm of complete solar cells sensitized with SQ 8 or SQ 12 and containing the Co-based electrolytes; normalized microsecond decays at 570 and 1550 nm of complete cells containing only ACN or the different Co-based electrolytes; cyclic voltammograms of SQ 8, SQ 12, and the different $[\text{Co}(\text{L})_3]^{3+/2+}$ complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the MINECO through projects PLE2009-0015 and MAT2011-25472. G.M. is grateful to MINECO for the “Juan de la Cierva” contract.

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