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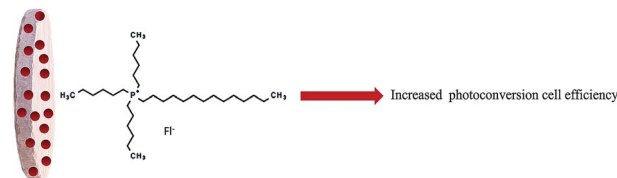
PAPER

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Dye-sensitized solar cells using fluorone-based ionic liquids with improved cell efficiency

Ana L. Pinto, A. Jorge Parola, João P. Leal, Isabel B. Coutinho* and Cláudia C. L. Pereira*

TiO₂ and [P_{6,6,6,14}]₂ fluorone highly hydrophobic ionic liquid dye.



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Dye-sensitized solar cells using fluorone-based ionic liquids with improved cell efficiency†

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Ana L. Pinto,^a A. Jorge Parola,^a João P. Leal,^{bc} Isabel B. Coutinho^{*d} and Cláudia C. L. Pereira^{id *a}

Six trihexyltetradecylphosphonium chloride (P_{6,6,6,14}Cl) based ionic liquids (IL) with dianionic fluorone derivatives were synthesized with total exchange of chloride from the dianionic dye: Fluorescein (a), Rose Bengal (b), Phloxine B (c), Eosin B (d), Eosin Y (e) and Erythrosine B (f). Spectroscopic characterization of these viscous salts indicated the presence of the expected 1 or 2 strong absorption bands. A total of 12 compounds, as sodium (from a to f) or as trihexyltetradecylphosphonium dianion salts (from a' to f'), were used for sensitization of nanocrystalline TiO₂. Here, we report the sensitization activity of these metal free dyes in terms of current–potential curve, open-circuit potential, fill factor, and overall solar energy conversion efficiency which have been evaluated under 100 mW cm⁻² light intensity. We developed a strategy to improve the light harvesting of these conventional dyes by simple cationic exchange which was accompanied by a minimum of 30% increase in the cell photovoltaic conversion efficiency. Also, for Eosin B the binding to TiO₂ apparently allows reduction of the –NO₂ electron-withdrawing group to –NO₂²⁻. This provides a new interaction between the reduced nitro group and the TiO₂ surface, reflecting an improvement in the overall DSSC performance reaching its maximum of 0.85% efficiency after light DSSC soaking. Factors that improve DSSC performance like aggregate inhibition, increment of the electrode's quasi-Fermi level and slight red shift in the absorption spectra of the tested anionic dyes were achieved by simple cationic exchange.

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1 Introduction

Dye Sensitized Solar Cells (DSSCs) are now acknowledged as economically viable photovoltaic systems and may actually represent a low-cost alternative to traditional crystalline silicon photovoltaics, silicon-based heterojunction solar cells (Si-HJT) with energy conversion up to 26.6%.¹

Many efforts have been made to change the different parts of organic dyes to optimize DSSC performance.

Sun and co-workers reported an increase in dye efficiency using a NO₂ group that attaches to the TiO₂ surface despite its electron withdrawing character.² This “auxiliary anchor” concept is not exclusive to nitro groups; it has for instance been observed in other anchoring groups such as the hydroxyl group or tetrazoles.³

Bio-inspired structures for photo-electrical conversion DSSCs exist in nature, where organisms developed an efficient strategy to improve light capture by using special molecular units called light harvesting antennas. These units comprise several pigments whose role is to collect incident solar photons at different wavelengths and to taper them through efficient energy transfer steps into a single molecular unit which in turn triggers the photoinduced electron transfer chain.⁴ Natural light harvesting antennae consist of chromophores such as chlorophylls, carotenoids, lutein, *etc.* Chlorophylls have a very high molar extinction coefficient (approx. 100 000 M⁻¹ cm⁻¹) owing to their highly conjugated monomeric units. The first application of the antenna effect in a hybrid photoelectrochemical device was reported by Scandola and co-workers as early as 1990 with the complex cyano-bridged trinuclear $\{[\text{Ru}(\text{bpy})_2(\text{CN})_2]_2\text{Ru}(\text{bpy}(\text{COO})_2)_2\}^{2-}$.⁵

The intrinsic photon capturing and associated photo-induced electron transfer properties, typical of porphyrin macrocycles, encouraged the idea of using these compounds as antennae in artificial photosynthesis.⁶ A number of efficient porphyrin sensitizers have been reported by Grätzel, Diau, Yeh, Lin, Wang, Imahori, and many other groups.⁷

Other bio-inspired photosensitizers are anthocyanins with great potential to be used in DSSCs.^{8,9} The first anthocyanin-

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based DSSC reported, cyanidin-3-glucoside, a natural dye extracted from blackberries, had a conversion yield of 0.56%.¹⁰

The photosensitization of TiO₂ semiconductors can also be accomplished by using other classes of metal-free organic dyes (fluorone, triarylmethane, azo and thiazine-based) as photosensitizers.^{11,12}

Structurally, fluorones consist of a xanthene ring with terminal oxygen atoms which is connected to a phenyl moiety through a quaternary carbon atom, which is known to be perpendicular to the xanthene moiety and therefore not π -conjugated with it.

These dyes have properties such as better anchorage to the TiO₂ surface, short adsorption time, chemical stability, and a wide visible spectrum which makes them promising candidates for use as sensitizers in dye-sensitized solar cells.

Molecular organization of dianionic fluorone core derivatives, including large size, a moderate degree of symmetry, and delocalized charge, should favor the formation of an IL, when combined with trihexyltetradecylphosphonium chloride, a cation that easily forms ionic liquids with a broad array of anions.¹³

Fluorescence and UV-vis spectroscopic studies of this family of fluorescein core ionic liquids when dispersed in an aqueous medium as nanodroplets indicate the formation of strongly fluorescent J-type aggregates together with weakly fluorescent monomeric forms.¹⁴

Various investigations have been carried out on modified oxide semiconductor photoanodes with doped metal nanoparticles,¹⁵ non-metal materials,¹⁶ cation or anion adsorption,¹⁷ *etc.*, aiming to enhance the overall light to electricity conversion efficiency of these devices.

In this work, six fluorone dianionic compounds were tested as sensitizers and the influence of the countercation of the dye on the DSSC performance was evaluated. Also, the presence of a withdrawing -NO₂ group in one of these structures that may be reduced upon light exposure of the TiO₂ attached dye highlights the possibility of a strong interaction between the reduced nitro group and the TiO₂ surface. The light exposure effect provides a way to significantly and irreversibly improve solar cell efficiency. Moreover, it creates an opportunity to study some of the most fundamental limiting factors of dye-sensitized solar cells.

A light exposure effect has been reported for various dye sensitized systems.¹⁸ Oligothiophene ruthenium sensitizers presented a 30% improvement in the power conversion efficiency after 12 days of light exposure at 60 °C and 1 sun accompanied by a considerable improvement in both J_{sc} and V_{oc} .¹⁹ Based on a red shift of the spectral response of the solar cells, the authors suggested the possible rearrangement of the thiophene unit under the light soaking conditions.

In DSSCs ionic liquids have been used essentially as redox mediators in dye sensitized solar cell electrolyte systems.²⁰⁻²³

Our main objective was to develop a new strategy to improve DSSC performance by simple cationic exchange of any anionic dyes. We purposely selected previously reported highly aggregable compounds, with simultaneous low photoconversion

efficiency dyes, to more clearly evaluate the achieved improvement.

Therefore, in this study, we have investigated the effect of cation exchange of anionic compounds on the overall cell performance parameters of six different fluorone dyes as [P_{6,6,6,14}]⁺ ionic liquids, which according to our literature overview are the first ionic liquid dyes used for sunlight energy conversion studies.

2 Experimental

The fluorone (Fl) dyes reported in this study are Fluorescein (a), Rose Bengal (b), Phloxine B (c), Eosin B (d), Eosin Y (e) and Erythrosin Y (f) with structural formulae shown in Fig. 1.

IL salts of type [P_{6,6,6,14}]₂Fl were prepared by a standard halide metathesis reaction between disodium salts of dyes (a-f) and trihexyltetradecylphosphonium chloride (P_{6,6,6,14}Cl) as previously described.^{12,24} Full exchange of sodium was confirmed by elemental analysis, nuclear magnetic resonance spectroscopy and electrospray mass spectrometry.

2.1 Materials and instruments

Sodium salt dyes (Aldrich) were used as received; [P_{6,6,6,14}]⁺Cl⁻ (Cytec), methanol (Aldrich, p.a.) and CDCl₃ solvent were purchased from Cambridge Isotopes.

Optical measurements. The UV-vis absorption spectra of the solutions and the dyes adsorbed onto TiO₂ in transmittance mode were recorded by using a Varian Cary 5000. All the spectra were collected at room temperature.

2.2 DSSC fabrication and photovoltaic characterization

The overall power conversion efficiency of a photovoltaic device is one of the most important parameters in solar cell research, and is defined by the short-circuit photocurrent density (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor (FF), and the incident light power (P_{in}):

$$\eta = \frac{J_{sc} V_{oc} FF}{P_{in}}$$

The conductive FTO-glass (TEC7, Greatcell Solar) used for the preparation of the transparent electrodes was first cleaned with detergent and then washed with water and ethanol. To prepare the anodes, the conductive glass plates were immersed in a TiCl₄/water solution (40 mM) at 70 °C for 30 min, washed with water and ethanol and sintered at 500 °C for 30 minutes. The TiO₂ nanocrystalline layers were deposited on the FTO plates by screen-printing transparent titania paste (18NR-T, Greatcell Solar) using a frame with polyester fibres having 43.80 mesh per cm². This procedure, involving two steps (coating and drying at 125 °C), was repeated two times. The TiO₂ coated plates were gradually heated up to 325 °C, and then the temperature was increased to 375 °C in 5 minutes, and afterwards to 500 °C. The plates were sintered at this temperature for 15 min, and finally cooled down to room temperature. Afterwards the TiO₂ film was treated with the same TiCl₄/water

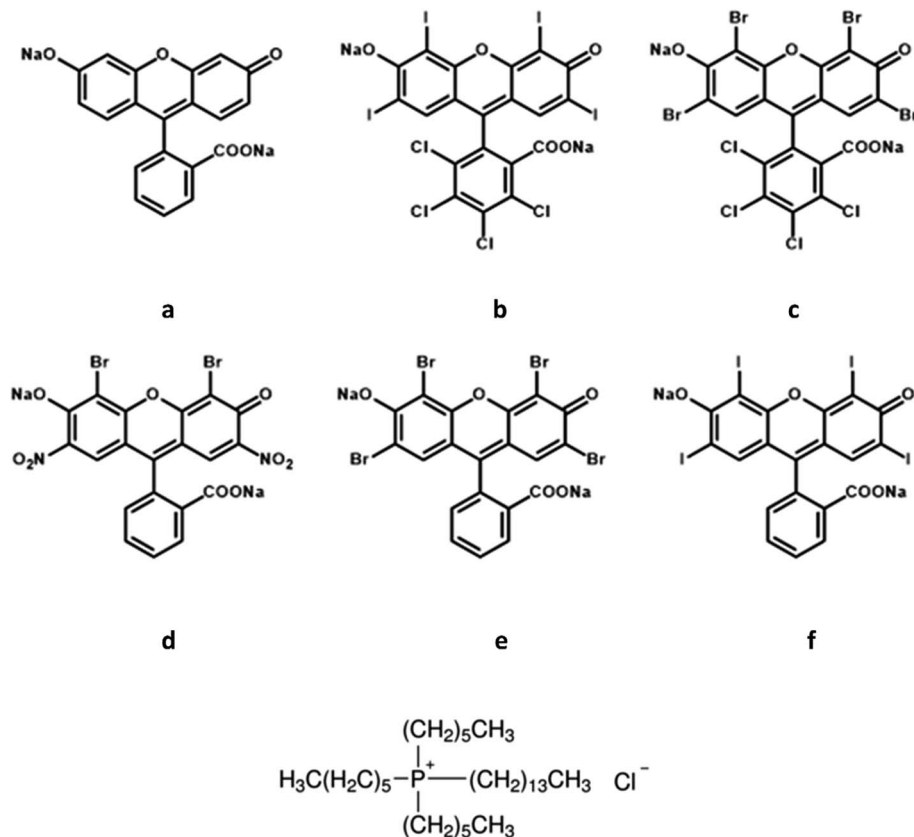


Fig. 1 Organic dyes from a to f (as disodium salts) used in the synthesis of $[P_{6,6,6,14}]^+$ ILs.

solution (40 mM), following the procedure previously described. A coating of reflector titania paste (WER2-O, Greatcell Solar) was deposited by screen-printing and sintered at 500 °C. Each anode was cut into rectangular pieces (area: 2 cm × 1.5 cm) having a spot area of 0.196 cm² with a thickness of 15 μm. The titanium oxide film employed for UV-vis absorption experiments was prepared by the doctor blade method: two edges of the glass plate were covered with stripes of adhesive tape (3 M Magic) in order to obtain a transparent ultrathin TiO₂ film with an estimated thickness of about 6 μm. Dye solutions of the fluorone salts (0.5 mM) were prepared in methanol. The photoanodes were prepared by soaking the screen-printed glass overnight (~17 h) in the different dye solutions, at room temperature in the dark. The excess dye was removed by rinsing the photoanodes in the same solvent as that employed in the dye solution.

Each counter-electrode consisted of an FTO-glass plate (area: 2 cm × 2 cm) in which a hole (1.5 mm diameter) was drilled. The perforated substrates were washed and cleaned with water and ethanol in order to remove any residual glass powder and organic contaminants. The Pt transparent catalyst (PT1, Greatcell Solar) was deposited on the conductive face of the FTO glass by the doctor blade method: one edge of the glass plate was covered with a strip of adhesive tape (3 M Magic) both to control the thickness of the film and to mask an electric contact strip. The Pt paste was spread uniformly on the substrate by sliding a glass rod along the tape spacer. The adhesive tape strip was

removed, and the glass was heated at 550 °C for 30 min. The photoanode and the Pt counter-electrode were assembled into a sandwich type arrangement and sealed (using a thermopress) with a hot melt gasket made of Surlyn ionomer (Meltonix 1170-25, Solaronix SA).

The electrolyte was prepared by dissolving the redox couple, I⁻/I₂ (0.8 M LiI and 0.05 M I₂), in an acetonitrile/valeronitrile (85 : 15, % v/v) mixture. The electrolyte was introduced into the cell *via* backfilling under vacuum through a hole in the back of the cathode. Finally, the hole was sealed with adhesive tape.

For each compound, three cells were assembled under the same conditions, and the efficiencies were measured 10 times for each one resulting in 30 measurements per compound.

3 Results and discussion

The ILs were synthesized *via* a two-step synthesis. Two equivalents of trihexyltetradecylphosphonium chloride ($P_{6,6,6,14}Cl$) were added to a solution of Fluorescein (a), Rose Bengal (b) Phloxine B (c), EosinB (d), EosinY (e) and Erythrosine B disodium salts (f) dissolved in methanol. After one hour of stirring the solvent was evaporated under reduced pressure and the crude oily material was extracted with dichloromethane.¹² The characterization of all six viscous materials is consistent with the structures of the precursors presented in Fig. 1 as $[P_{6,6,6,14}]^+$ salts. These room temperature ionic liquids will be referred hereafter to as a' to f'.

The material thermal properties were evaluated with no detection of the melting point between $-100\text{ }^{\circ}\text{C}$ and $+100\text{ }^{\circ}\text{C}$ (see the ESI†).

3.1 Absorption behavior of the material

All spectra (a–f and a'–f') exhibited the typical features of fluorones in a dianion state, *i.e.* a strong band and a much weaker one at *ca.* 500 nm.

Band splitting has been observed in concentrated solutions of fluorescein dianions (a) due to the formation of dimers and trimers (as shown in Fig. 2a). For instance, in basic aqueous solutions, dimer formation results in two absorption bands, at ~ 505 and 470 nm, while trimer formation yields a spectrum of three bands at ~ 505 , 470 , and 457 nm (with the shape of a shoulder).²⁴

The electronic absorption spectra of the films (right side of the spectra) display bands in the visible region (400–700 nm) of electromagnetic spectra. The absorption peak values (λ_{max}) are presented in Table 1, when adsorbed on a $6\text{ }\mu\text{m}$ TiO_2 film, as sodium (a–f) and as $[\text{P}_{6,6,6,14}]^+$ (a'–f') salts (Fig. 2).

The most noticeable feature is the progression of bands that are slightly enhanced over what is observed for b–e, when Na^+ is exchanged with $[\text{P}_{6,6,6,14}]^+$ (b'–e').

This observation agrees with the overall DSSC performance improvement from a–e to a'–e' and will be further discussed.

The most intense absorption band has been attributed to the π – π^* transition of fluorescein's xanthene ring. The lower energy for b' to e' may be attributable, at least in part, to the enhanced vibronic structure induced by a more rigid environment in these halofluoresceins,²⁵ when compared with b–e. Such an effect may arise from enhanced coulombic interactions between fluorones and $[\text{P}_{6,6,6,14}]^+$ as well as its viscosity/microfluidity.

For b and c, the iodine and bromine atoms make the xanthene ring more electron rich while its chlorine atoms make the phenyl much more electron poor, leading to the electron push–pull effect. This effect strengthens the electronic overlapping between the two π -systems and lowers the energy of the S1 excited state which corresponds to higher absorption wavelengths.²⁶

The broadening of the optical absorption spectra and their red-shifting are indications of adsorption interaction between the dye and the semiconductor surface (Fig. 2). As can be seen, the shifting in the TiO_2 film to lower energy values is more pronounced for $[\text{P}_{6,6,6,14}]^+$ salts compared with their Na^+ equivalent, although the same qualitative behavior is maintained.

In DSSCs, H- or J-aggregates of dyes are usually formed during device fabrication, when the solvent evaporates. After adsorption onto the TiO_2 layer, they create a solid dye- TiO_2 film that comprises the DSSC photoanode.

Dye aggregates are characterized by broadening of the absorption spectra. For H-aggregates the spectrum shifts to lower wavelengths (hypsochromic) while for J aggregates it shifts to higher wavelengths (bathochromic) when compared to the monomer absorption band.²⁷ This behavior was observed for $[\text{P}_{6,6,6,14}]^+$ fluorone dyes, with increment of λ_{max} , when

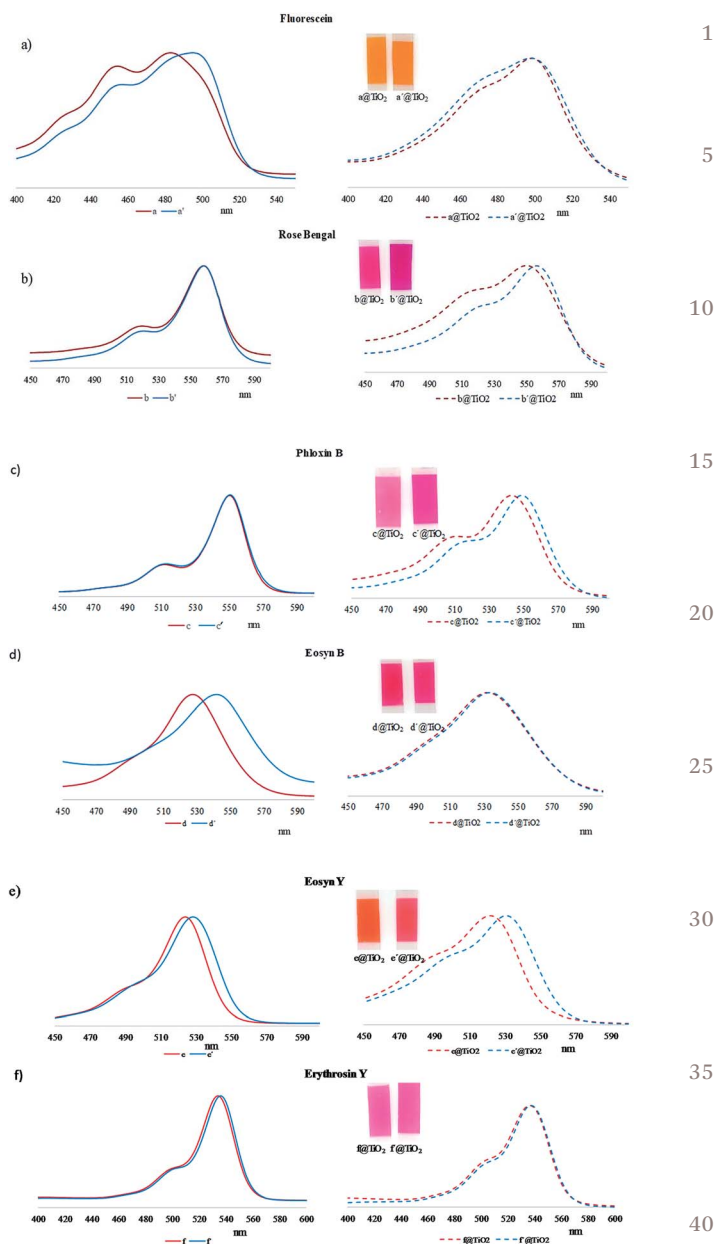


Fig. 2 UV-vis absorption spectra of a–f and a'–f' in ethanol (column on the left) and solutions of 5×10^{-4} M adsorbed on a $6\text{ }\mu\text{m}$ TiO_2 film (column on the right). Abs(au) versus λ (nm).

Table 1 Main bands in the absorption spectra of a–f and a'–f' adsorbed on a TiO_2 film in EtOH

Compound	Absorption bands (nm)	Compound	Absorption bands (nm)
a	471, 498	a'	471, 498
b	521, 550	b'	521, 556
c	509, 543	c'	517, 549
d	522	d'	529
e	490, 522	e'	497, 531
f	506, 537	f'	506, 537

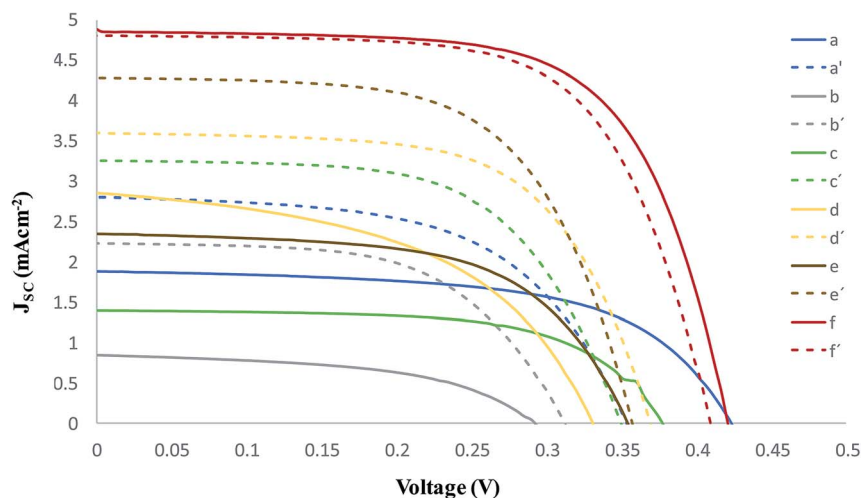


Fig. 3 J - V curves of DSSCs based on dyes **a-f** and **a'-f'** measured under AM 1.5 solar light (100 mW cm^{-2}), using 0.8 M LiI and 0.05 M I_2 in acetonitrile : valeronitrile ($85 : 15, \% \text{ v/v}$) as the electrolyte. Linear lines correspond to **a-f** dyes as disodium salts and dotted lines represent the results for the corresponding $[\text{P}_{6,6,6,14}]^+$ dianionic compounds, **a'-f'**.

Table 2 Photovoltaic performance parameters of DSSCs based on fluorone dyes **a-f** (sodium fluorone salts) and **a'-f'** (tri-hexyltetradecylphosphonium fluorone salts) under 100 mW cm^{-2} simulated AM 1.5 illumination. The results presented are for the best performing cell. N719 is the benchmark

Dye	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	η (%)
a	0.44	1.9	0.63	0.53
a'	0.38	2.80	0.61	0.66
b	0.28	1.06	0.55	0.17
b'	0.31	2.22	0.58	0.41
c	0.40	1.98	0.64	0.51
c'	0.35	3.25	0.61	0.7
d	0.31	2.36	0.46	0.33
d'	0.37	3.59	0.63	0.65
e	0.34	3.07	0.62	0.66
e'	0.36	4.23	0.61	0.94
f	0.42	4.9	0.67	1.39
f'	0.41	4.8	0.66	1.31
N719	0.44	18.5	0.53	4.44

adsorbed on the TiO_2 surface compared to the dilute dye solution (left side spectra in Fig. 2), where we assume the absence of aggregates. In contrast, λ_{max} is lower when Na^+ salts are adsorbed, suggesting that for these dyes H aggregates are preferably formed. This was clearly observed for Rose Bengal (Fig. 2) and Phloxine B dyes, which curiously are more prone to dye aggregation due to their halide-substituted phenyl ring.²⁸ Apparently, the presence of $[\text{P}_{6,6,6,14}]^+$ reduces the tendency of formation of H-aggregates as can be concluded from the absorption spectra (Fig. 2b) with λ_{max} very close to that of the monomeric species.

3.2 Photovoltaic performance of DSSCs

DSSCs were fabricated using different photoanodes consisting of either Na^+ (**a-f**) or $[\text{P}_{6,6,6,14}]^+$ (**a'-f'**) dianionic fluorones adsorbed on TiO_2 structures.

The photocurrent-voltage plots for DSSCs assembled with fluorone dyes, **a-f** and **a'-f'**, are shown in Fig. 3.

For **f**, Na^+ exchange with $[\text{P}_{6,6,6,14}]^+$ did not produce any increment in DSSC performance, as was observed for the other fluorones (**a-e**). We considered that a bulkier halogen atom, like iodine, in **f** produces a very uniform distribution of the conjugated electronic system of their xanthene groups. This suggests a larger contribution of dispersion forces in the heavy halogenated xanthene aggregates, leading to a better alignment of their monomeric units.²⁹ This can be clearly observed through analysis of the UV-vis spectra of **f** and **f'** in solution and when confined in TiO_2 films (Fig. 2f). Here, λ_{max} is the same in diluted solution, exclusively with monomeric composition, and when the dyes are adsorbed on the anode surface.

This may suggest that for the remaining tested dyes (**a-e**), the increment in DSSC performance may be directly related to the reduction of H-aggregates, when adsorbed on the anode surface.

The short circuit photocurrent density J_{sc} , open-circuit photovoltage V_{oc} , fill factor FF, and efficiency η derived from photocurrent-voltage measurements of different types of DSSCs are summarized in Table 2. From **a** to **e** and **a'** to **e'**, DSSC performance parameters have an overall tendency of improving photovoltaic cell efficiency.

As seen from Fig. 3 and Table 2, Erythrosine (**f**) shows the highest photocurrent ($J_{sc} = 4.90 \text{ mA cm}^{-2}$) and the highest energy conversion efficiency ($\eta = 1.3\%$). The decreasing trend of cell efficiencies of the experimented fluorone based dyes is as follows: Rose Bengal (**b**) < Fluorescein (**a**) \approx Phloxine B (**c**) < Eosin B (**d**) < Eosin Y (**e**) < Erythrosine (**f**).

Depending on the nature of the substituent, the xanthene sub-unit acts as an electron acceptor (or donor), while the phenyl moiety is the corresponding electron donor (or acceptor) in photoinduced electron transfer (PET). The remote substitution in the phenyl ring is still capable of affecting the fluorescence characteristics, especially the fluorescence quantum yield and lifetime.³⁰

Table 3 Photocurrent efficiency improvement after cation exchange for the anions a–f (%)

Fluorone	η improvement (%)
a	39%
b	141%
c	37%
d	91%
e	42%
f	$\approx 0\%$

V_{oc} is the difference between the redox level of the electrolyte and the quasi-Fermi level of the semiconductor; it can be affected by the concentration of electrons in the conduction band (CB) of the semiconductor and the magnitude of electron recombination from the injected dyes to the oxidized electrolyte.

Small cations, like Na^+ , are more readily adsorbed onto the TiO_2 electrode than the cations having larger sizes like $[\text{PC}_{6,6,6,14}]^+$, and in return, on the Na^+ positively charged TiO_2 surface a downward shift in the Fermi level occurs.

Hence, a drop in V_{oc} occurs due to the positive shift of the conduction band edge induced by the presence of surface Na^+ .³¹ This effect was clearly observed for dyes **b**, **d** and **e**, which have higher photoelectron conversion efficiency improvement (Table 3).

The Fill Factor (FF) is a measure of the quality of the device. FF varies with different fabrication methods, characterization conditions, and the series resistance.³²

The most straightforward way to increase J_{sc} is to absorb a greater fraction of the incident light. Extending the dye's absorption into near-infrared is an option for increasing the photocurrent density.³³ This was observed for a–e fluorone dyes

after cationic exchange, with a maximum absorption red-shift of 6 nm for Rose Bengal (**b**), notably the dye which presented the highest photocurrent efficiency improvement (141%) (Table 3).

We used N719, di-tetrabutylammonium *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II), as the benchmark to control the relative quality of the overall results.

3.3 Nitro effect

An interesting phenomenon was found when measuring the photoelectric properties of DSSCs fabricated with Eosin B (**d** and **d'**) under simulated AM 1.5 G illumination (100 mW cm^{-2}). Initially, the efficiencies were comparably low (*ca.* 0.16% for **d** and 0.33% for **d'**). After a period of device testing, the efficiencies of DSCs increased approximately two-fold to 0.65% ($J_{sc} = 3.59 \text{ mA cm}^{-2}$, $V_{oc} = 0.59 \text{ V}$, and $\text{FF} = 0.66$, Fig. 4).

It was previously reported that continuous light exposure provides a way to significantly and irreversibly improve solar cell efficiency.³⁴ TiO_2 works as a photobleaching catalyst, which promotes photocatalytic oxidation of the dye.³⁵ According to the literature, it is likely, that there is a weak interaction between the nitro group and the TiO_2 surface when **d** and **d'** are adsorbed *via* the carboxylate group.³⁶ This brings it in close contact with the semiconductor surface and if reduced to NO_2^{2-} , the nitro group provides a means of other electronic coupling of the molecule to the TiO_2 surface increasing the ease of electron injection from the sensitizer to the conduction band of TiO_2 , ultimately increasing all DSSC parameters.³⁷

For compounds **d** and **d'**, light exposure resulted in simultaneous improvements in the short-circuit current density (J_{sc}), the open-circuit voltage (V_{oc}), the fill factor (FF) and consequently the photoelectrochemical conversion efficiency (η) (Table 4).

From the six different tested fluorone core dyes, after a period of device testing of approximately 3 minutes that

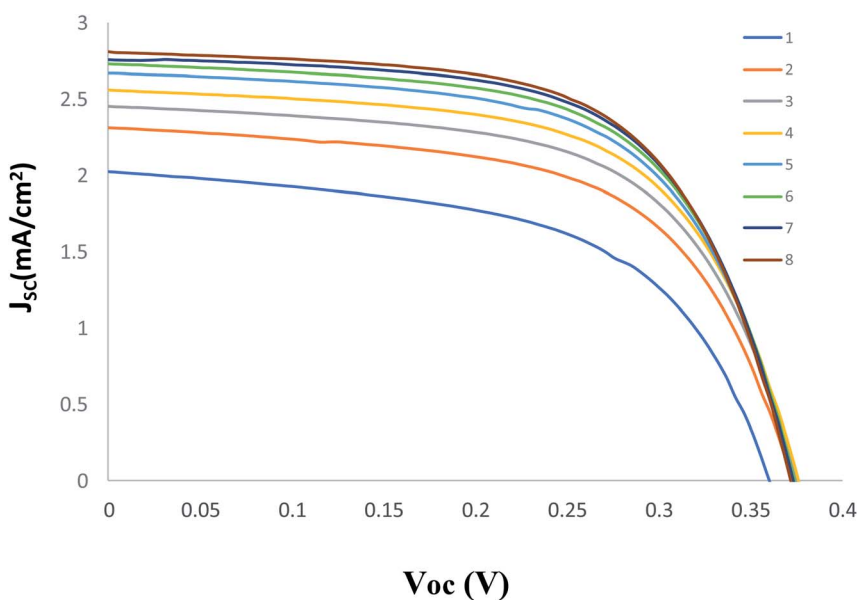


Fig. 4 Photovoltaic performances of DSCs of **d'** upon successive light exposure. Each measurement corresponds to 16 s under the solar light simulator.

Table 4 DSSC parameter behaviour of **d** and **d'** upon light exposure for the first and fifth measurements. Each measurement corresponds to 16 s of light exposure

Compound	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	η (%)
d -1 st measurement	0.25	1.69	0.37	0.16
d -5 th measurement	0.31	2.36	0.46	0.34
d' -1 st measurement	0.34	2.0	0.49	0.33
d' -5 th measurement	0.37	2.8	0.63	0.65

correspond to ten consecutive measurements, the efficiencies of DSSCs increased approximately 112% for **d** and 100% for **d'** achieving a maximum of 0.34% for **d** and 0.65% for **d'** (Fig. 4).

The electron-withdrawing group, NO₂, causes a red-shift in the absorption spectra (Fig. 2); 5-nitro provides a positive charge to the phenyl and an electric attraction to the xanthene, which stabilizes the xanthene and decreases the energy gap between the HOMO and LUMO (red shift). The results of investigation indicate that for 3-(2-(5-(2-cyano-4-nitrophenyl)thiophen-2-yl)-5-(dihexylamino)phenyl)propanoic acid the nitro group attaches to the TiO₂ surface, causing bleaching of the dye absorption but increasing the ability of the dye to inject electrons into the conduction band of TiO₂.

A red shift from 522 nm and 530 nm for **e** to 529 nm and 543 nm for **d** was observed for the most intense bands compared to the full xanthene brominated analogue, eosin Y (**e**). When the extra anchoring mode is achieved, the final photo-electrochemical conversion efficiency is 0.34% for the disodium salt and 0.65% for the diphosphonium equivalent.

4 Conclusion

Here we present and discuss a simple strategy for DSSC performance optimization when anionic fluorone dyes are used for sensitization. The effect of long chain phosphonium cations on the DSSC cell parameters can be compared to that of the pre-adsorption technique used to improve the overall efficiency of a DSSC over conventional photoanodes, especially those using smaller cations. A hydrophobic environment for the device is also recommended to minimize the direct contact between the electrolyte and anode, reducing the recombination rate too, since long alkyl chains repel iodide from the TiO₂ surface.

We suggest an easy strategy for reducing aggregate formation and simultaneously increasing the electrode's quasi-Fermi level (which will result in an increase in V_{oc}) and in some cases a red-shift of fluorone anionic dyes, which together contribute to an overall improvement from 37 to 141% in energy conversion efficiency.

For one of the selected dyes, an overall increase in photo-conversion efficiency was observed upon repeated light exposure. This interesting result was previously reported in the literature although very little exploited, and is a subject to be explored by us in the near future.

Conflicts of interest



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