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Electron injection *versus* charge recombination in photoelectrochemical solar cells using *cis*-$[(dcbH_2)_2Ru(CNpy)(H_2O)]Cl_2$ as a nanocrystalline TiO_2 sensitizer

Christian Graziani Garcia[a], Adelino Kaoru Nakano[a], Cornelis J. Kleverlaan[b], Neyde Yukie Murakami Iha[a,*]

[a] *Instituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes, 748-05508-900 Sao Paulo, SP, Brazil*
[b] *Dipartimento di Chimica, Università di Ferrara, Via Luigi Borsari, 46-44100 Ferrara, Italy*

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Abstract

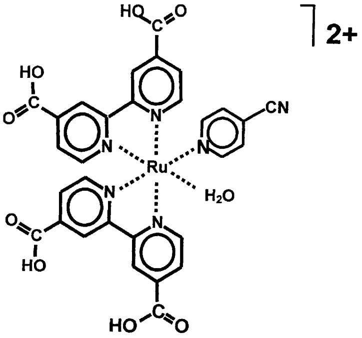
A transparent photoanode was prepared by immobilizing *cis*-$[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$ ($dcbH_2$: 4,4′-$(CO_2H)_2$-2,2′-bipyridine; and CNpy: 4-cyanopyridine) in a TCO substrate coated with nanocrystalline TiO_2 film for incident monochromatic photon-to-current conversion efficiency (IPCE) measurements. Time-resolved experiments were carried out and electron injection across the excited dye/semiconductor interface, as well as charge recombination and quenching processes were investigated. Transient absorption difference spectra revealed the formation of the oxidized complex $[(dcbH_2)_2Ru(III)(CNpy)(H_2O)]$ upon light excitation. The recovery is a multiphasic process attributed to a charge recombination of the injected electron across the semiconductor/dye interface in the microsecond time domain. The presence of iodide results in a much faster quenching of the oxidized complex. Thus, an appropriate concentration of donor species in the redox mediator is essential to effectively recover the sensitizer closing the electric circuit so that a dye-sensitized solar cell works in a regenerative regime. Therefore, under proper experimental conditions, the compound performs successfully as the molecular sensitizer in photoelectrochemical solar cells based on dye sensitization of nanocrystalline n-type TiO_2. Kinetics data of electron injection obtained by time-resolved experiments for *cis*-$[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$ are discussed along with the properties of the sensitizer in photoelectrochemical solar cells.

Keywords: Photoelectrochemical solar cell; 4-Cyanopyridine; Transient absorption spectra; Time-resolved spectroscopy

1. Introduction

Photoelectrochemical solar cells based on dye sensitization of wide band gap semiconductors, referred to as dye cells, perform an efficient conversion of visible light into electricity. Electron injection from the excited dye molecule into the semiconductor conduction band is achieved with energy lower than the band gap energy, enabling a better match with the solar spectrum for practical applications. Light absorption stands apart of the charge separation process. Therefore, electron–hole recombination and the well-known deleterious features presented by traditional colored semiconductors are prevented [1–7].

Ruthenium(II) polypyridyl complexes with carboxylated ligands are commonly employed as a TiO_2 sensitizer in such cells [8–13]. These compounds present intense MLCT bands in the visible region overlapping the solar spectrum, combined with suitable photoelectrochemical properties and stability in the Ru(III) oxidized state. The carboxylic groups permit the necessary contact and electronic coupling between the sensitizer and TiO_2 surface resulting in an ultra fast electron transfer from the dye into the semiconductor [2,6,9,14,15]. When anchored to a nanocrystalline semiconductor, the sensitizer performs efficient light harvesting and provides an enhanced spectral response of the TiO_2 electrodes to visible light.



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* Corresponding author. Fax: +55-11-3815-5579.
E-mail address: neydeiha@quim.iq.usp.br (N.Y. Murakami Iha).

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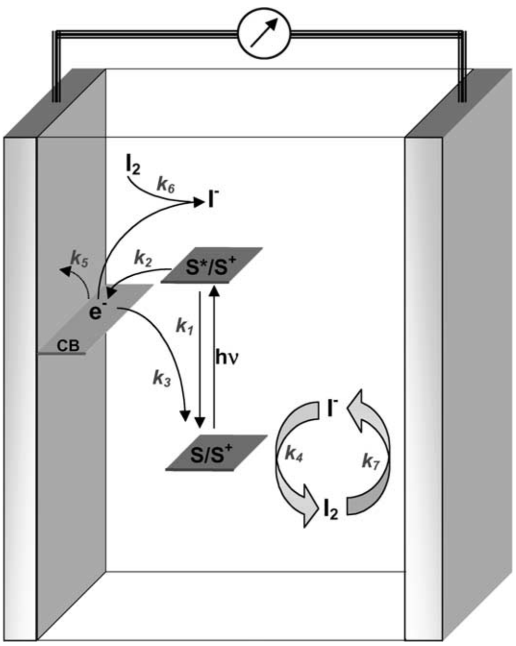

Scheme 1. Schematic representation of the photoconversion process in dye-sensitized solar cells. S: *cis*-$[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$, and CB: conduction band.

The established mechanism of energy conversion in regenerative dye-sensitized solar cells is shown in Scheme 1 [15–18]. Following light absorption, the excited dye S^* promotes electron injection into the semiconductor conduction band, keeping the electron–hole pair separated by the semiconductor/sensitizer interface. The oxidized sensitizer is reduced by the reduced form of a redox mediator couple, the oxidized form of which, in turn, migrates toward the counter electrode to be reduced, closing the redox cycle. The theoretical voltage output, which can be achieved is limited to the difference between the redox potential of the mediator couple and the quasi-Fermi level of the semiconductor. Actual performance of the cells is directly dependent on the different electron transfer processes involved. Losses in efficiency can occur by radiative and non-radiative decay of the excited state, by recombination of electrons in TiO_2 with oxidized dye molecules and by reactions of electrons in TiO_2 with oxidants in solution [15–18].

Previous investigations employing a series of *cis*-$[(dcbH_2)_2RuLL']$ species, where $dcbH_2$ is 4,4′-$(CO_2H)_2$-2,2′-bipyridine and L and/or L′ are substituted pyridines, as n-TiO_2 sensitizers resulted in efficient photoelectrochemical solar cells [19–23]. The nature of the ancillary ligands L/L′ coordinated to the non-attached side of the dye affects the resulting properties of the sensitizers enabling the tuning of the spectral sensitivity to the visible light and the overall conversion efficiency of the cells. Interestingly, heteroleptic derivatives with different ancillary ligands presented better spectral response and performed more efficiently as molecular sensitizer in the cells [20,23].

In order to further examine this system, excited state properties of the complex having one 4-cyanopyridine as an ancillary ligand, *cis*-$[(dcbH_2)_2Ru(CNpy)(H_2O)]Cl_2$, attached to TiO_2 films, were investigated. The processes of charge recombination and quenching following the electron transfer across the excited dye/semiconductor interface were examined through time-resolved experiments carried out with the sensitizer anchored to nanostructured TiO_2 films.

2. Experimental

All chemicals were reagent grade or of the best commercially available purity. HPLC solvents and reagent grade water were always used. Transparent TiO_2 films for photoelectrochemical measurements were obtained following the procedure described in the literature [9,24]. The semiconductor emulsion was deposited on a conductive fluorine-doped SnO_2 glass for the cell performance measurement. The molecular sensitizer *cis*-$[(dcbH_2)_2Ru(CNpy)(H_2O)]Cl_2$ was synthesized as previously described [23] and attached to the TiO_2 surface by immersing the processed electrode for 1–3 h in approximately 1×10^{-4} M ethanolic solution of the ruthenium complex.

2.1. Methods

Absorption spectra were recorded on a Hewlett-Packard HP 8453 UV–VIS spectrophotometer. Emission measurements were performed on a SPEX Fluoromax 2 spectrofluorometer equipped with a Hamamatsu R3896 tube.

Transient absorption measurements were performed using a set-up and an apparatus that have been previously described using a 7 ns pulse at 532 nm from a Continuum Surelight Nd:Yag laser [25]. The measurements were performed in 0.3 M $LiClO_4$ in acetonitrile, which is frequently used in photoelectrochemical experiments.

Photoelectrochemical measurements were performed by using the dye-sensitized TiO_2 photoanode in a transparent thin layer sandwich-type solar cell as previously described [20,23]. The photoanode consists of a FTO substrate with the TiO_2 film sensitized by the dye. The counter electrode presents a transparent platinum film on its conductive surface. The mediator electrolyte, 0.03 M I_2/0.3 M LiI solution in acetonitrile, is sandwiched between the two electrodes.

Initial performance of the cells was evaluated employing a system comprising of a 200 W Hg (Xe) arc lamp and interference filters, as detailed elsewhere [26]. Photocurrent and voltage measurements, as well as photoaction spectra, were obtained as previously described [15,19,20].

3. Discussion

Fig. 1 shows the electronic absorption spectra of the TiO_2-covered TCO substrate in the absence and presence

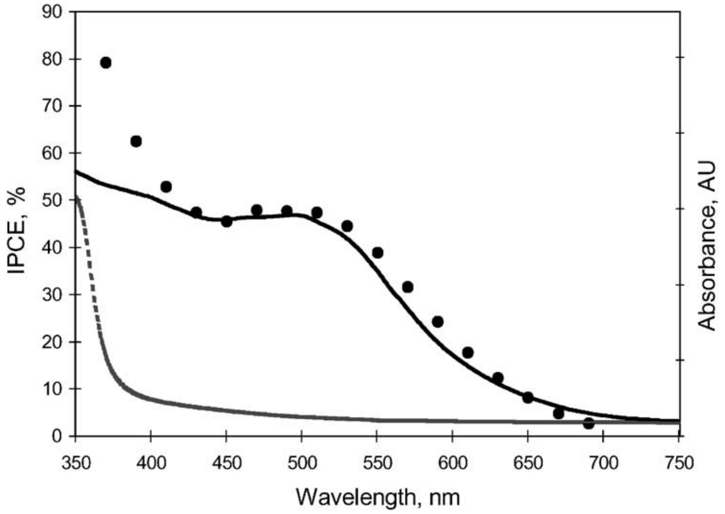

Fig. 1. Absorption spectra of TiO_2 (- - -) and $[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}/TiO_2$ (—) in acetonitrile at room temperature. Photocurrent action spectrum (●) obtained with transparent thin layer solar cell employing the compound as the molecular sensitizer.

of *cis*-$[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$ onto its surface and the photocurrent action spectrum obtained with a transparent thin layer solar cell employing the photoanode with the compound as the molecular sensitizer. The electrode spectrum resembles the absorption spectrum of the corresponding molecular sensitizer in solution. Analogous to similar complexes, it displays intense MLCT ($d\pi \rightarrow \pi^*$) bands in the visible region, as well as intra-ligand ($\pi \rightarrow \pi^*$) transitions in the UV region [9,10,12,15,19,20,23,27–29].

The action spectrum closely matches the spectrum of the dye adsorbed on the electrode. The heteroleptic derivative *cis*-$[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$ with different ancillary ligands performs efficient sensitization of nanocrystalline n-TiO_2 in photoelectrochemical solar cells, with high incident monochromatic photon-to-current conversion efficiency (IPCE) values in the visible light region [24].

Fig. 2 presents the transient absorption difference spectra of the TiO_2 film covered with *cis*-$[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$ in acetonitrile. Following light absorption, the electron injection from the excited sensitizer into the semiconductor results in the formation of the oxidized complex *cis*-$[(dcbH_2)_2Ru(III)(CNpy)(H_2O)]^{3+}$. The bleaching in the 360–600 nm region is attributed to depletion of the ground state MLCT absorption [4,15,25,30–36]. As can be seen in Fig. 2, injected electrons recombine with the oxidized dye without the presence of an active redox mediator. The absence of positive absorption in the 350–400 nm region, assigned to intra-ligand transitions in the excited sensitizer, confirms that electron injection into the semiconductor takes place within the laser pulse (<10 ns or faster), which is in agreement with earlier reported data [25,31,34,36,37]. The absorption in wavelengths higher than 600 nm arises from the oxidized Ru(III) complex with a possible contribution from the electron injected into the semiconductor [31,35–38].

Emission spectrum of *cis*-$[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$ in solution exhibits a band centered at 680 nm, assigned to a radiative decay of the triplet excited state, $^3[(dcbH_2)_2Ru(CNpy)(H_2O)]^*$, formed after excitation of *cis*-$[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$. The short-lived ($t < 5$ ns) weak emission could not be resolved with the available equipment.

Changes in absorbance of *cis*-$[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$ measured at 480 nm following excitation after 3.0 mJ cm^{-2} laser pulse at 532 nm are presented in Fig. 3. Electron injection results in fast bleaching followed by the regeneration of the ground state absorbance of *cis*-$[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$. The recovery process observed in Fig. 3A is associated with the reduction of the oxidized

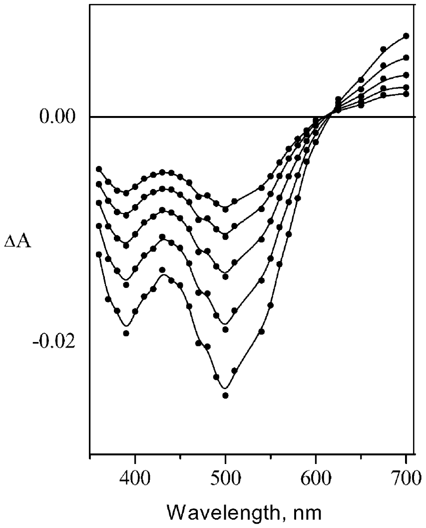

Fig. 2. Absorption difference spectra of $[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$ on TiO_2 film in acetonitrile (0.3 M $LiClO_4$) at room temperature; $t_d = 0$, 50, 250, 1000 and 2000 ns; $\lambda_{exc} = 532$ nm, 3.0 mJ cm^{-2} laser pulse.

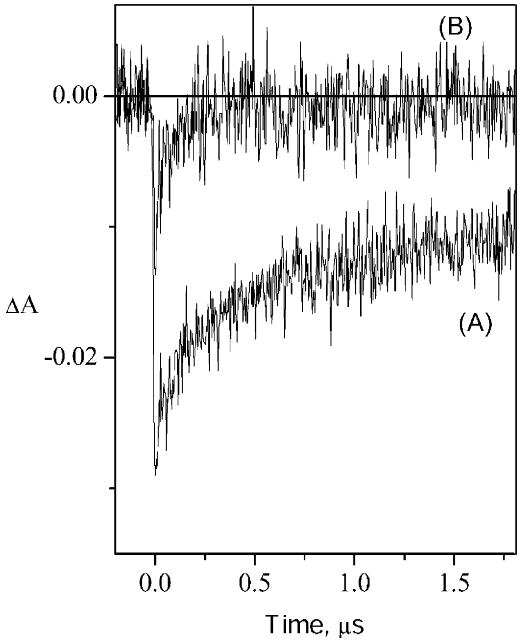

Fig. 3. Kinetics of $[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$ recovery on TiO_2 followed at 480 nm in: (A) acetonitrile (0.3 M $LiClO_4$), and (B) acetonitrile (0.3 M LiI); $\lambda_{exc} = 532$ nm, 3.0 mJ cm^{-2} pulse.

species, $[(dcbH_2)_2Ru(III)(CNpy)(H_2O)]^{3+}$, formed after excitation and electron injection [15,25,30,33]. The regeneration process presents a comparatively fast step followed by another slower one showing a complex kinetics. Such behavior is often observed in similar heterogeneous systems and is attributed to multiple electron trapping in surface defects, which could delay the recovery process [15,30,32,34,35,37,39–42].

Fig. 3B shows the recovery process in the presence of an active electrolyte, the iodide ion. The concentration employed (0.3 M LiI) is the same as in regular photoelectrochemical solar cell experiments and Li^+ concentration is unchanged with respect to the recombination experiments (0.3 M $LiClO_4$, Fig. 3A). One can observe that in the presence of iodide (Fig. 3B), the recovery process is much faster than in its absence (Fig. 3A). The presence of iodide promotes a fast quenching of the oxidized species recovering the reduced dye, as observed in Fig. 3B, before other side reactions, such as photosubstitution can take place. Such behavior is found to be dependent on the concentration of iodide [39]. Slow dye regeneration is found to be a limiting factor, which restricts the conversion efficiency in photoelectrochemical solar cells [18]. Therefore, a proper concentration of the reducing mediator is required.

After light absorption, the primary step of electron injection across the sensitizer/semiconductor interface is extremely fast. The oxidized dye must be promptly reduced by an electrolyte relay in solution to prevent electron recombination or any photodegradation reactions. Reduction of the oxidized sensitizer by iodide (Eq. (1)) regenerates the chromophore to its original state, concluding the cycle initiated with light absorption.

$$2[(dcbH_2)_2Ru(III)(CNpy)(H_2O)]^{3+} + 3I^- \rightarrow 2[(dcbH_2)_2Ru(II)(CNpy)(H_2O)]^{2+} + I_3{}^- \quad (1)$$

The wavelength-dependent IPCE-term evaluates the overall photoconversion process. It is directly related to three parameters, namely, light harvesting efficiency, LHE (the fraction of radiant power absorbed by the sensitizer), the quantum yield for charge injection into the semiconductor (ϕ) and the efficiency of electron collection in the external circuit (η) (see Eq. (2))

$$\mathrm{IPCE}(\lambda) = \mathrm{LHE}(\lambda)\phi\eta \quad (2)$$

LHE relates to the active surface area of the semiconductor and to the light absorption cross-section of the sensitizer. This term depends on the active surface coverage and on the dye molar extinction coefficient [9,11,43].

The η-value is related to the fraction of injected electrons, which achieves the back contact of the photoanode through the semiconductor layer [11,43]. Both electron percolation through the external circuit (k_5) and recombination of electrons in the conduction band with oxidized sensitizer (k_3) or the oxidized relay electrolyte (k_6) will limit the magnitude of the η-parameter. This parameter can be estimated by the recovery of the sensitizer in the presence (k_4) or absence (k_3) of iodide according to the expressions below. Simplified formulae (Eqs. (5) and (6)) are obtained with the assumption that all kinetics are pseudo-first-order [25,43].[1]

$$\eta = \frac{k_4[I^-]}{k_3[e^-] + k_4[I^-]} \quad (3)$$

or

$$\eta = 1 - \frac{k_3[e^-]}{k_3[e^-] + k_4[I^-]} \quad (4)$$

$$\eta = \frac{k_4}{k_3 + k_4} \quad (5)$$

or

$$\eta = 1 - \frac{k_3}{k_3 + k_4} \quad (6)$$

These equations express the competition between the quenching process promoted by the relay electrolyte (k_4) and the recombination of electrons in the conduction band with the oxidized sensitizer (k_3) [15,25]. Therefore, the magnitude of the η-parameter can be estimated from kinetics measurements, by Eqs. (5) and (6), and from Eq. (2) by using steady-state measurements.

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[1] See [25] for the derivation of the kinetic processes.

Table 1
Parameters determined from time-resolved and steady-state experiments for the calculation of the η-term for several $(dcbH_2)_2RuLL'$ sensitizers

L/L'	Time-resolved			Steady-state			References
	$k_3 \times 10^6$ [a]	$(k_3 + k_4) \times 10^6$ [b]	η_{calc} [c]	$IPCE_{max}$ [d]	LHE_{max} [e]	η_{calc} [f]	
$CNpy/H_2O$	10 (70)–0.27 (30)	45	0.78	0.60	0.96	0.63	This work
ppy/ppy	5 (65)–0.23 (35)	15	0.67	0.56	0.91	0.62	[15]
4-ppt	14.7 (55)–0.4 (45)	66.7	0.78	0.74	0.90	0.82	[25]
2-ppt	11.6 (55)–0.4 (45)	62.5	0.81	0.73	0.97	0.75	[25]
Bpzt	8.5 (43)–0.3 (57)	71.4	0.88	0.80	0.98	0.82	[25]
2-ppzt	8.8 (49)–0.3 (51)	38.4	0.77	0.68	0.99	0.69	[25]

Values in parentheses are in percentage.

[a] Kinetic data from traces (A) of Fig. 3.

[b] Kinetic data from traces (B) of Fig. 3, $k_{obs} = k_3 + k_4$.

[c] Calculated from Eq. (6).

[d] Corrected for light absorption by the TCO glass.

[e] $LHE = 1 - 10^{-A}$, where A is the absorbance of the dye on the TiO_2 layer (see [9,25]).

[f] Calculated from Eq. (2), with $\phi = 1$.

Table 1 summarizes these parameters for the determination of the η-term obtained for photoanodes constituted by $[(dcbH_2)_2Ru(II)(CNpy)(H_2O)]Cl_2$ onto TiO_2. The quenching of Ru(III) by I^- (Fig. 3B) was treated as a single exponential process. Traces of the recombination between the electron in the semiconductor conduction band and the oxidized sensitizer (k_3) were fitted with a bi-exponential function, due to the presence of a fast ($k \approx 1 \times 10^7\,s^{-1}$) and a slow ($k \approx 3 \times 10^5\,s^{-1}$) component. Only the fast component is considered, since the quenching of Ru(III) is completed within 100 ns. Table 1 also presents the data previously reported with similar sensitizers with different ancillary ligands, such as 4-phenylpyridine (ppy) [15] and a series of triazole ligands: 3-(2-hydroxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole (2-ppt), 3-(4-hydroxyphenyl)-5-(pyridin-2-yl)-1,2,4-triazole (4-ppt), 3,5-bis(pyrazin-2-yl)-1,2,4-triazole (bpzt), and 3-(2-hydroxyphenyl)-5-(pyrazin-2-yl)-1,2,4-triazole (2-ppzt) [25].

It is observed from Table 1 that the values obtained for the η-term by time-resolved experiments are reasonably similar to those obtained by steady-state experiments. Nonetheless, care must be taken in analyzing these values, as a result of the assumptions and simplifications employed in Eqs. (5) and (6). The quenching efficiency calculated for $[(dcbH_2)_2Ru(CNpy)(H_2O)]Cl_2$ by using the parameters determined in time-resolved experiments ($\eta = 0.78$) is higher than that obtained for the similar compound with ppy as ancillary ligand ($\eta = 0.67$) [15]. Experiments with both sensitizers were performed on optically matched TiO_2 photoanodes. The result is in accordance with the higher IPCE-values in the 400–500 nm region for the CNpy complex when compared with its analogous ppy derivative. Such a correlation between both η- and IPCE-parameters is expected, since the efficiency of the cells is partially attributed to the interplay between the recombination of electrons of the conduction band with the oxidized sensitizer and the quenching of Ru(III) by the electrolyte relay [25]. The relationship between both the parameters is further observed along the data reported for other sensitizers (Table 1). The higher quenching efficiency values obtained with the set of triazole complexes is accompanied by IPCE-values superior to those presented by the CNpy and ppy derivatives. Fig. 4 presents the relationship between both η- and IPCE-parameters for the series of mentioned sensitizers. A linear correlation and ascendant behavior show that the η-values are closely related with the IPCE, which is expected since both reflect the conversion efficiency.

The kinetics of back electron transfer to the oxidized sensitizer in the microsecond time domain contrast to the ultra fast electron injection. The former is avoided due to the fast regeneration of the sensitizer by the redox relay in solution. A successful performance of dye-sensitized photoelectrochemical solar cells is mostly attributed to the different time scale between both interfacial electron transfer processes [4,33]. The obtained LHE factor close to unity presented in Table 1 is a critical factor for the photoconversion process, since the device should be able to collect as much incident light as possible.

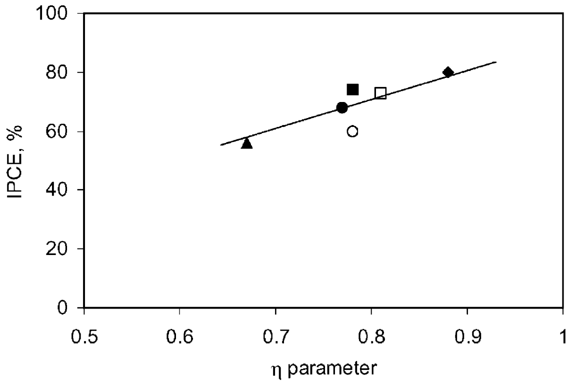

Fig. 4. Relationship between IPCE and η-values from time-resolved experiments for several $(dcbH_2)_2RuLL'$ sensitizers. $L/L' = CNpy/H_2O$ (○), ppy/ppy (▲), 4-ppt (■), 2-ppt (□), Bpzt (◆) and 2-ppzt (●).

4. Conclusion

Time-resolved experiments with nanocrystalline n-type TiO_2 sensitized by $[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$ led to important kinetic data related to the photoelectrochemical solar cell performance. The efficient capture of the oxidized dye by the electron relay in solution directs the electron transport process to the desired pathway preventing the recombination of the injected electron with the oxidized sensitizer. The adequate concentration of donor species in the redox mediator provides a rapid regeneration of the oxidized dye, which is critical to the electrical circuit, as well as to the stability of the dye-sensitized solar cell. The different order of magnitude between the processes of electron injection and charge recombination are essential for the successful operation of the photoelectrochemical solar cells. The analysis of experiments on TiO_2 photoanodes functionalized with $[(dcbH_2)_2Ru(CNpy)(H_2O)]^{2+}$ and other species has shown a linear correlation between the quenching efficiency η- and the IPCE-parameters.

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