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Efficient passivated phthalocyanine-quantum dot solar cells†

Vicente M. Blas-Ferrando,[a] Javier Ortiz,[a] Victoria González-Pedro,[b]
Rafael S. Sánchez,[b] Iván Mora-Seró,[b] Fernando Fernández-Lázaro[a] and
Ángela Sastre-Santos*[a]

The power conversion efficiency of CdSe and CdS quantum dot sensitized solar cells is enhanced by passivation with asymmetrically substituted phthalocyanines. The introduction of the phthalocyanine dye increases the efficiency up to 45% for CdSe and 104% for CdS. The main mechanism causing this improvement is the quantum dot passivation. This study highlights the possibilities of a new generation of dyes designed to be directly linked to QDs instead of the TiO$_2$ electrodes.

Dye-sensitized solar cells (DSSC) have emerged as low cost alternatives to silicon.[1] The most frequently used dyes are ruthenium complexes,[2] porphyrins,[3] and phthalocyanines,[4] although eventually quantum dots[5] are attracting more and more attention.

Quantum dots (QDs) are nanocrystals of semiconductor materials undergoing the phenomenon of quantum confinement.[6] They are heat resistant, low cost materials that can efficiently transfer electrons to large band gap semiconductors and whose electronic properties can be tuned by controlling the particle size, shape and composition.[7] Moreover, they are quite promising light harvesting materials in DSSCs because of their ability to generate multiple charge carriers[8] under high energy irradiation and to inject hot electrons allowing to potentially overcome the theoretical limit of Shockley–Queisser.[9] However, the efficiencies achieved with QD-sensitized solar cells (QDSCs) are much lower (6–7%)[10] than those obtained with DSSCs (13%).[11] Although the photocurrent is comparable in both devices, the voltage and the fill factor for QDSCs are lower due to the existence of electron transfer processes working against the cell cycle.

Various strategies have been used to increase the efficiency of QDSC devices, such as doping of the semiconductor with transition metal ions[12] or the use of plasmon resonances in metallic nanoparticles to generate charge carriers in adjacent semiconductor materials.[13] The most extensively used semiconductor quantum dots, such as CdSe or CdS, only absorb in the visible range. If a near infrared-absorbing dye was attached to this kind of quantum dot, the resulting structure could maximize the absorption of radiation and, in addition, reduce internal recombination, thus enhancing the photoinjected charge from the QD in a synergic process.[14] In this way, bilayer electrodes[15] sensitized with quantum dots and dyes or colloidal quantum dots acting as antennae that funnel absorbed light to the dye molecules via Förster resonance energy transfer (FRET) have been used.[16] Alternative strategies such as supersensitization of CdS QDs with a near-infrared organic dye[17] and sensitization of TiO$_2$ films with covalently linked squaraine-CdSe quantum dots[18] have improved the performance of QDSCs. Despite QDSCs and DSSCs following the same working principles, there is a fundamental difference between both. QDs present surface states that may play an important role in the recombination process and, consequently, in the final device performance.[19,20] Photoexcited electrons and holes in QDs can recombine through QD surface states before being injected reducing the expected device photocurrent.[19] On the other hand, electrons photoinjected into TiO$_2$ can also recombine before they arrive to the extracting contact. Again, surface states in QDs can favor this recombination that reduces the device open circuit potential.[21] In this sense, efficient passivation of QD surface states is a strategy commonly employed to enhance QDSC performance.[19,21,22]

Phthalocyanines (Pcs) are aromatic macroheterocycles which have been used successfully in DSSCs because they absorb intensely in the red spectral region, are able to inject into titanium oxide and are thermal and photochemically very stable compounds.[23] Their tendency to form aggregates on the TiO$_2$ surface, which reduces the efficiency of solar cells, can be countered with the introduction of bulky groups in the peripheral[24] or apical[25] positions going to efficiencies up to 6.5%.[26]

The chemical coordination of QDs to the Pc ring has not received much attention. FRET from QDs to different phthalocyanine photosensitizers has been demonstrated in a number of studies[27] where Pcs and QDs were unlinked.[28] Until now, just

[a] Área de Química Orgánica, Instituto de Bioingeniería, Universidad Miguel Hernández, 03202 Elche, Spain. E-mail: asastre@umh.es; Fax: +34-966658405; Tel: +34-966658408

[b] Grup de Dispositius Fotovoltaics i Optoelectrónics, Departament de Física, Universitat Jaume I, 12071 Castelló, Spain. E-mail: sero@uji.es

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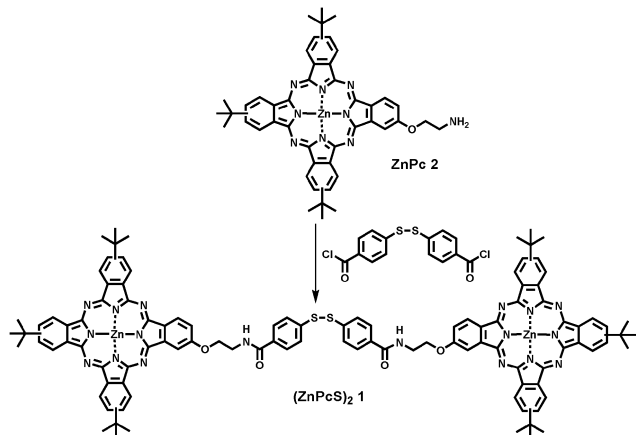
Scheme 1 Synthesis of bisphthalocyanine (ZnPcS)$_2$ **1**.

a few articles have been published where the QDs are covalently linked to the Pcs showing efficient FRET[29] but no QD-DSSCs have been studied yet.

Here we present the improvement in the efficiency of QDSCs through their passivation with covalently linked phthalocyanines. Our approach represents a seminal work for the development of a new generation of dyes with multifunctional purposes, completing the light absorption range of QDs and, at the same time, passivating the QD surface, enhancing consequently the contribution from QD sensitization. For this purpose, a new bisphthalocyanine (ZnPcS)$_2$ **1** containing two asymmetrically substituted Pcs has been synthetized (Scheme 1). (ZnPcS)$_2$ **1** presents a disulfide group for the covalent binding to QDs and bulky *tert*-butyl substituents to hinder possible aggregation.

(ZnPcS)$_2$ **1** was prepared by acylation of the aminoethoxy-phthalocyanine **2**[30] with 4,4′-dithio-bis-benzoyl chloride[31] in 96% yield (Scheme 1).

The UV-vis absorption of the bisphthalocyanine (ZnPcS)$_2$ **1** represented in Fig. 1a corresponds to a non-aggregated metallo-phthalocyanine exhibiting the typical sharp Q band transition at 675 nm, with vibronic replica at 610 nm, and a Soret band at around 350 nm. This behaviour is quite important for effective sensitization of the dye.[32] The normalized fluorescence spectrum is given in Fig 1a (red curve) being roughly mirror symmetric with respect to the absorption spectrum. From the intersection of the normalized absorption and emission spectra, the zero–zero excitation energy (E_{0-0}) is determined[33] as 1.82 eV.
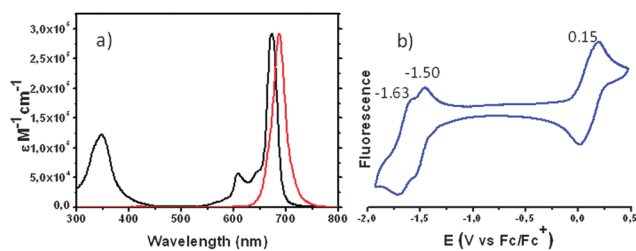

Fig. 1 (a) UV-Vis and fluorescence spectra of (ZnPcS)$_2$ **1** in DMF as solvent. (b) Cyclic voltammogram (100 mV s^{-1}) of 0.5 mM (ZnPcS)$_2$ **1** in benzonitrile as solvent containing 0.10 M of TBAPF$_6$ as supporting electrolyte.
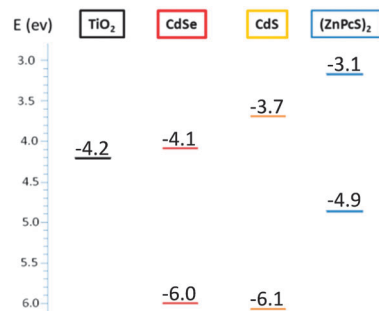

Fig. 2 Energy levels of TiO$_2$, CdSe, CdS and (ZnPcS)$_2$.

Cyclic voltammetric studies of (ZnPcS)$_2$ **1**, performed on a benzonitrile solution containing 0.10 M of TBAPF$_6$ as supporting electrolyte, showed an oxidation peak at 0.49 V and two reduction peaks at −1.13 V and −1.29 V *vs.* SCE (Fig. 1b). The electrochemically calculated HOMO–LUMO gap ($E_{ox} - E_{red}$), 1.63 eV, is roughly in agreement with the E_{0-0} energy, previously inferred from spectroscopic measurements.

The electrochemical characterization allows us to determine the energy of the HOMO orbital and, together with the 0–0 transition energy, the energy of the LUMO orbital. Taking into account these values, together with the energy value for the conduction band of TiO$_2$ (−4.2 eV), an energy level diagram can be sketched and the driving forces for electron injection and regeneration processes evaluated (Fig. 2). The LUMO position for (ZnPcS)$_2$ **1** is higher in energy than the conduction band (CB) of the CdSe and CdS QD, which is a fundamental requisite in order to achieve the electron injection from the excited dye to the QD thermodynamically.

Our study began with CdSe QDs. They were prepared by the successive ionic layer adsorption and reaction (SILAR) method on TiO$_2$ substrates, see ESI.† Half of these electrodes were immersed in a solution of the (ZnPcS)$_2$ **1** during 24 h while the rest were used without this treatment. The comparison of the parameters of solar cells assembled with the Pc-treated electrodes and those of solar cells assembled with the Pc-untreated electrodes will provide a measure of the efficacy of this protocol (Table 1). First, we studied the influence of the solvent in the process: chloroform, toluene and DMF were tested. Chloroform resulted in the worst results (entry 2). Change to toluene provided some improvements in cell parameters (entries 3 and 4). DMF, much more polar than the previous solvents, was then tested obtaining the best results with a significant increase in the photocurrent and voltage, increasing the efficiency to 2.9% (entry 5).

Fig. 3a shows the *J/V* curve comparing the Pc-untreated CdSe device as reference, CdSe with DMF and with our CdSe–(ZnPcS)$_2$ hybrid system. To rule out that the improvements were an effect of the solvent used in the process, the Pc-untreated reference electrode was treated with DMF (entry 6), obtaining a solar cell with an efficiency of 2.22% (Fig. 3a).

Higher V_{oc} and J_{sc} were obtained when (ZnPcS)$_2$ **1** was attached to the CdSe quantum dot. However, Fig. 3b (external quantum efficiency *versus* wavelength) does not show the expected improvement in the absorption area of phthalocyanines (600–700 nm).

Table 1 Values obtained from the devices

Entry	QD–ZnPc	Solvent	t (h)	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF	η (%)	EQE^{a} (%)
1	CdSe	—	—	8.25	422	56	2.00	35
2	CdSe–ZnPc **1**	CHCl$_3$	24	—	—	59	0.50	—
3	CdSe–ZnPc **1**	Tol	12	5.35	400	63	1.34	—
4	CdSe–ZnPc **1**	Tol	24	6.87	405	60	1.55	—
5	CdSe–ZnPc **1**	DMF	24	9.98	453	60	2.90	64
6	CdSe	DMF	24	9.02	430	54	2.22	40
7	CdS	—	—	4.85	461	59	1.30	37
8	CdS–ZnPc **1**	DMF	24	7.35	488	55	2.00	68
9	CdS	DMF	24	5.93	510	51	1.50	50
10	ZnPc **1**	DMF	—	0.29	196	52.5	0	—

^{a} λ_{max} = 535 nm for CdSe and λ_{max} = 440 nm for CdS.
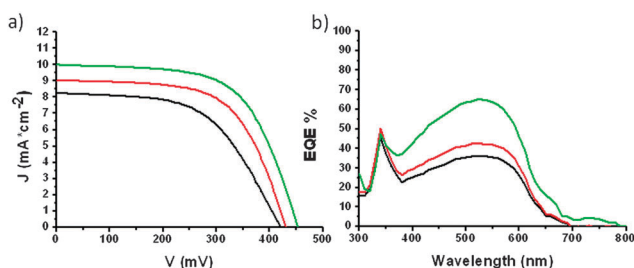

Fig. 3 (a) J/V curve of the QDSC device. (b) IPCE of the device: black line CdSe ref, red line CdSe–DMF and green line QD CdSe–ZnPc.

In addition, CdS-based QDSCs were also analyzed using the previous methodology. Electrodes were prepared in the same way as those of CdSe. When one of these electrodes was treated with (ZnPcS)$_2$ **1** solution in DMF for 24 h, a substantial increase in the photocurrent and improved fill factor and voltage were achieved, doubling the cell efficiency (entries 7 and 8 and Fig. 4a). Also, we rule out that the improvements were due to the effect of the solvent, obtaining a solar cell with an efficiency of 1.5% (entry 9, Fig. 4a). In order to discard that the direct sensitization of TiO$_2$ by (ZnPcS)$_2$ **1** was the major contribution to the photovoltaic response, a CdS-QD-free electrode was prepared adsorbing directly (ZnPcS)$_2$ **1** onto TiO$_2$ (entry 10). No efficiency was observed, ruling out this possibility.

Fig. 4b shows the plot of EQE vs. wavelength for these cells. A significant increase of the EQE in the area between 300 and 500 nm is observed, however, the same does not occur in the area of 600–700 nm where the phthalocyanine absorbs. To make sure that the phthalocyanine is attached to the quantum
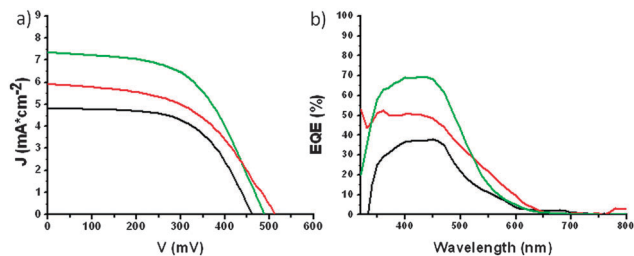

Fig. 4 (a) J/V curve of the QDSC device, (b) IPCE of the device. Black line CdS ref, red line CdS with DMF and green line QD CdS–ZnPc.
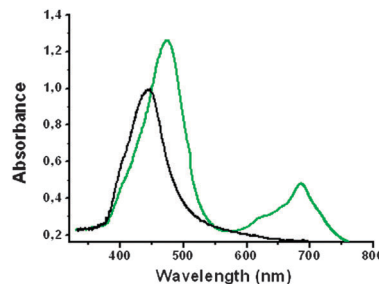

Fig. 5 Absorbance measurements of QD CdS ref black line, QD CdS–(ZnPcS)$_2$ green line.

dots, reflectance studies were conducted on the prepared electrodes. Fig. 5 shows the appearance of the absorption band typical of the phthalocyanines confirming their presence.

The observed increase of EQE in the light absorption region corresponding to CdS QDs indicates an effective beneficial interaction between QDs and dye molecules. We have also verified that the change in the absorption from the QDs (350–575 nm), see Fig. 5, for the QD CdS–(ZnPcS)$_2$ sample can only justify an increase of 10% in the photocurrent, but a much large increment of 52%, see Fig. 4b, is obtained. This fact together with the absence of EQE at the light absorption region of the dye suggest that the main effect of the interaction is the passivation of the QD surface.[22]

As has been commented previously, surface states in QDs can act as recombination centers of photoexcited electron–hole pairs, before electron injection into the electrode. Passivation of these states increases device IPCE and photocurrent.[19] In addition, electrons photoinjected into TiO$_2$ can also recombine through these QD surface states. This kind of recombination of electrons in TiO$_2$ will move down the TiO$_2$ Fermi level and, consequently, the cell photovoltage.[21] To this extent, passivation also enhances photovoltage and the FF.

In conclusion, we have successfully synthesized and characterized a new disulfide-bisphthalocyanine dye and we have explored its capacity as a superpassivating agent in QDSCs. With CdSe QDSCs we studied the effect of solvent on the process and concluded that the best one was DMF. Pc-treated QDSCs showed an improvement of the photocurrent that was not accompanied by a parallel increase of the IPCE in the absorption zone of the phthalocyanine. The QD:(ZnPcS)$_2$ hybrid provided a major improvement in photocurrent and voltage, concluding that the main effect of QD–dye interaction is the passivation of the QD surface. Reflectance studies confirmed the link of phthalocyanine molecules to quantum dots. The introduction of the phthalocyanine dye increases the efficiency up to 45% for CdSe and 104% for CdS. Further efficiency increase, currently under study, could be expected from the development of new dyes, linked to QDs either directly or through a conjugated bridge, which in addition can extend the light harvesting region. This study opens the possibility of design a new generation of dyes with an adequate functionalization to be directly linked to QDs boosting the solar cell efficiency by a synergic interaction in several ways, QD passivation and extended light harvesting.

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