

Dye sensitized solar cells using non-aggregated silicon phthalocyanines

Luis Martín-Gomis^a, Eva. M. Barea^{*b}, Fernando Fernández-Lázaro^{a◇}, Juan Bisquert^b and Ángela Sastre-Santos^{*a◇}

^a *División de Química Orgánica, Instituto de Bioingeniería, Universidad Miguel Hernández, 03202 Elche, Spain*

^b *Grup de Dispositius Fotovoltaics i Optoelectrònics, Departament de Física. Universitat Jaume I, 12071 Castelló, Spain*

Dedicated to Professor Karl M. Kadish on the occasion of his 65th birthday

Received 14 June 2011

Accepted 12 July 2011

ABSTRACT: Two new silicon phthalocyanines (SiPcs **1** and **2**) axially substituted with carboxylic acid appends have been synthesized and chemically characterized. DSC devices using SiPcs as sensitizers have been prepared for the first time. Although similar HOMO–LUMO values were obtained for both SiPcs, the device prepared with the SiPc **2** gives both higher open circuit voltage (V_{oc}) and also higher injection (j_{sc}), so the overall conversion efficiency is larger than for the one where SiPc **1** is used as a dye.

KEYWORDS: silicon phthalocyanines, dye sensitized solar cells.

INTRODUCTION

The use of sunlight to produce energy through photovoltaic devices appears to be one of the most attractive and challenging alternatives to conventional energy sources. The so-called Dye Sensitized Solar Cells (DSCs) are a new class of photovoltaic devices, formed by a TiO_2 anode coated with an organic dye [1]. This organic dye acts as an antenna, using solar radiation to be excited and, finally, injecting electrons in the conduction band of TiO_2 . These economic devices are believed to reduce the production costs, compared with standard silicon-based photovoltaic devices. There is still significant room for improvement. Thus, their design and the nature of its components can be changed and optimized in order to achieve better performances [2].

Although the DSC maximum conversion efficiency has traditionally been achieved with ruthenium-based dyes [3], it is worth mentioning the improvement reached

in efficiency and cell performance when more friendly stable π -aromatic compounds, such as porphyrins, are used as sensitizers [4]. However such dyes frequently lack of absorption in the far red/near IR, where solar radiation is most intense which is a severe limitation. On the other hand, phthalocyanines (Pcs) have strong absorption in this region and they are also known to have high chemical, thermal and optical resistances, making them ideal candidates as efficient dyes in DSC design [5]. However, Pcs, due to their planar aromatic structure, have a great tendency to form insoluble aggregates [6]. This intrinsic characteristic, in most cases, inhibits the properties presented by Pcs at the molecular level. One of the strategies employed to prevent the formation of phthalocyanine aggregates is the functionalization of the axial positions, whenever possible. In this context, taking advantage of the hexacoordinate nature of hypervalent silicon, it is possible to functionalize the axial valences in silicon-phthalocyanine (SiPc), yielding silicon phthalocyanine derivatives whose tendency to aggregation is minimal [7].

Recently, highly efficient light harvesting has been achieved in ternary blend solar cells consisted in

◇SPP full member in good standing

*Correspondence to: Ángela Sastre-Santos, email: asastre@umh.es, tel.: + 34 96665-8408, fax: + 34 96665-8351

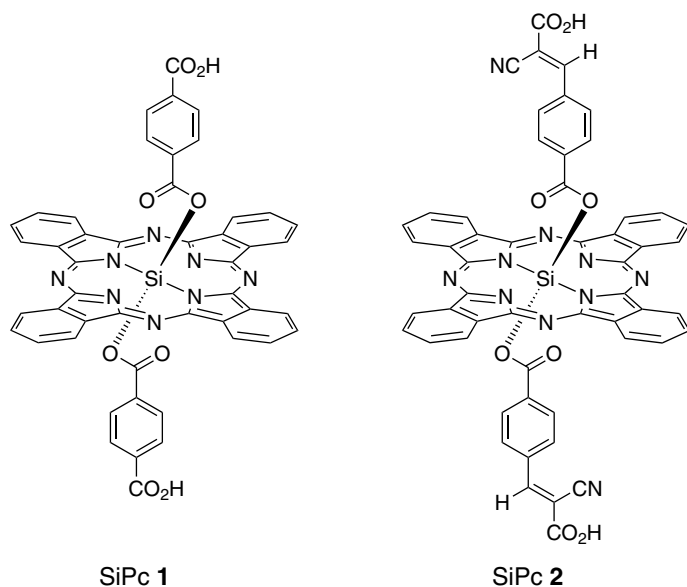


Chart 1. Silicon phthalocyanine derivatives **1** and **2**

poly(3-hexylthiophene) (P3HT), a fullerene derivative (PCBM), and a SiPc derivative as light-harvesting dye. The authors claimed that the SiPc molecules are selectively localized at the P3HT/PCBM interface with an interfacial coverage of 40% which is an ideal interfacial structure for the efficient photovoltaic conversion [8]. Also, it has been demonstrated that the use of a mixture of bis(trihexylsilyloxy)silicon phthalocyanine and bis(trihexylsilyloxy)silicon naphthalocyanine as near-IR dye in multi-colored dye-sensitized polymer/fullerene solar cells enhances the power conversion efficiency up to 4.3% compared to that of the individual ternary blend solar cell with a single dye [9]. However, to the best of our knowledge, just one example of silicon naphthalocyanine has been described so far as dye in DSCs devices [10]. For all these reasons, we consider that the use of SiPcs as dyes in DSCs should be explored.

Here, we present the synthesis and characterization of two new silicon phthalocyanine compounds, SiPc **1** and

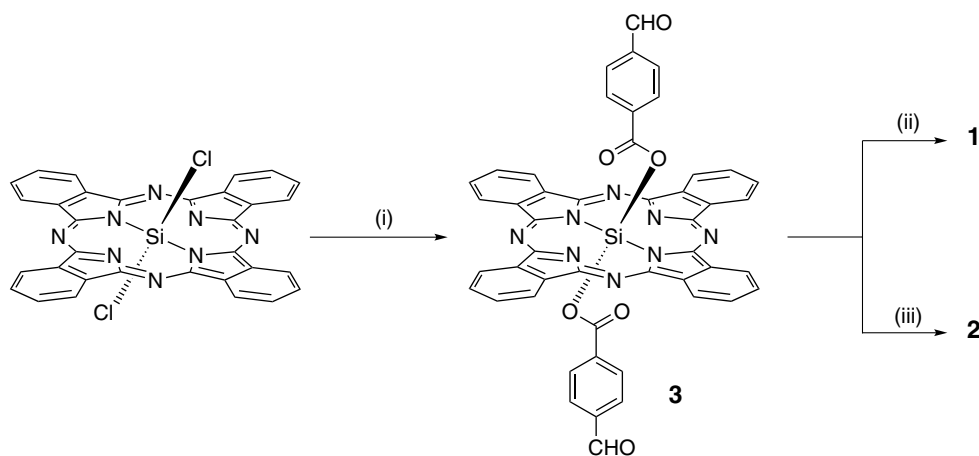
SiPc **2** (Chart 1), axially substituted with carboxylic acid appends. Preliminary studies about their sensitizing abilities in standard DSCs are also presented, showing efficient spectral sensitization of TiO₂ nanostructured photoelectrodes.

RESULTS AND DISCUSSION

Synthesis

The new silicon phthalocyanines **1** and **2** were synthesized as it is described in Scheme 1. Phthalocyanine **3**, axially substituted with formyl groups, was obtained through a condensation reaction between the commercially available dichlorosilicon phthalocyanine and excess of *p*-formylbenzoic acid. This phthalocyanine was used as starting compound for the synthesis of phthalocyanines **1** and **2**. Thus, oxidation of **3** with sodium chlorite and sulfamic acid gave **1** in 85% yield, while phthalocyanine **2** was accomplished, in a 50% yield, by Knoevenagel reaction with cyanoacetic acid.

SiPcs **1–3** were fully characterized by ¹H NMR, FTIR, UV-vis and HR-MALDI-TOF-MS. The ¹H NMR spectrum of SiPc **3** (Fig. 1c) shows two multiplets at 9.76–9.71 ppm and 8.44–8.40 ppm corresponding to the aromatic hydrogens of the phthalocyanine ring. Furthermore, there is a signal centered at 9.39 ppm, which integrates for two protons, assigned to the two hydrogen atoms of the formyl groups in the axial substituents. This signal belongs, together with the two doublets at 6.76 ppm and 5.25 ppm corresponding to the A₂B₂ aromatic system upfield-shifted due to the strong ring current effect of the Pc, to the axial benzoate groups. The ¹H NMR spectra of SiPcs **1** and **2** (Fig. 1a and b, respectively) show, as it has been already stated for the ¹H NMR spectrum of **3**, the signals corresponding to the aromatic phthalocyanine protons together with the corresponding upfield-shifted



Scheme 1. Synthesis of **1** and **2**: (i) 4-formylbenzoic acid, dyglime, 160 °C, 35%, (ii) sulfamic acid, sodium chlorite, THF/H₂O, rt, 85%, (iii) cyanoacetic acid, piperidine, DMF, 100 °C, 50%

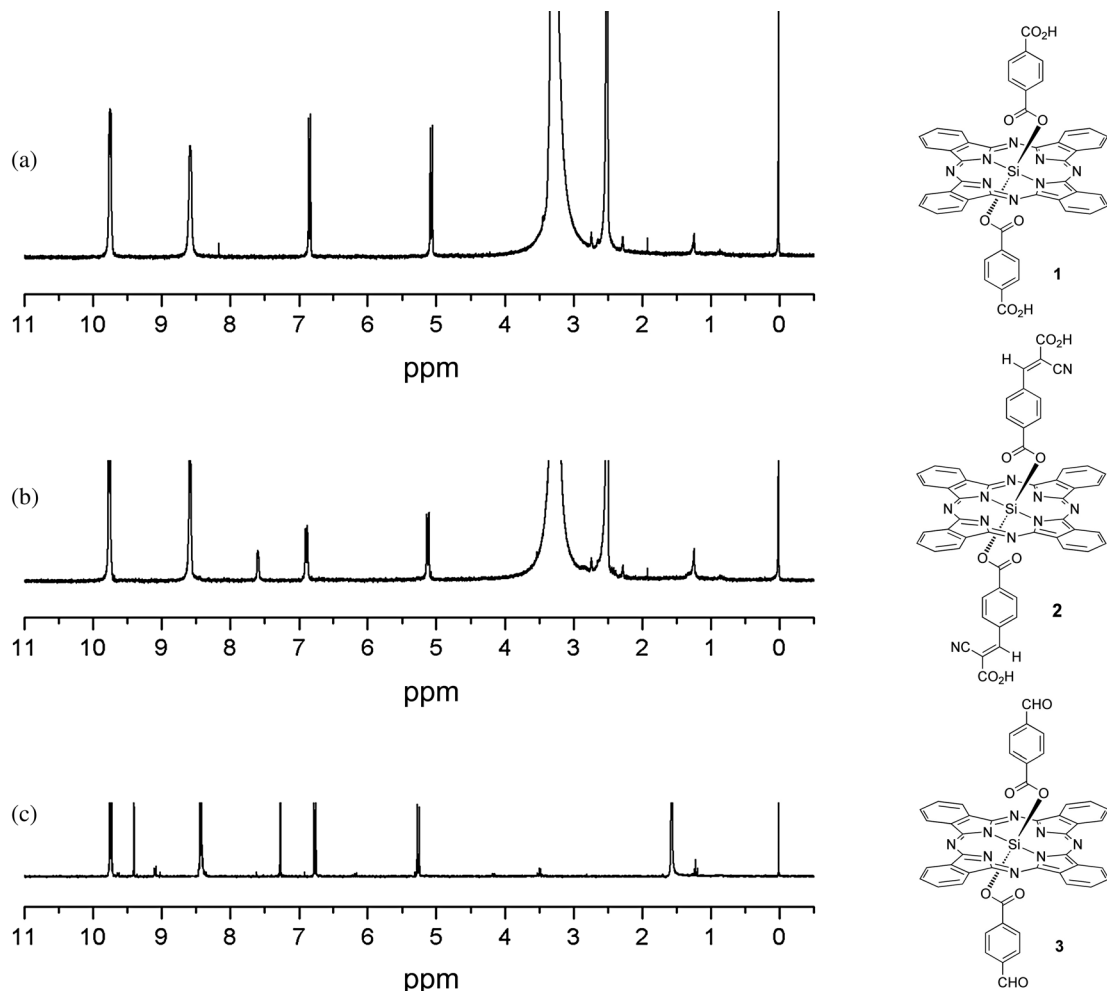


Fig. 1. ^1H NMR spectra of (a) SiPc **1** in $\text{DMSO}-d_6$ as solvent, (b) SiPc **2** in $\text{DMSO}-d_6$ as solvent and (c) SiPc **3** in CDCl_3 as solvent

aromatic benzoate hydrogens. Moreover, a broad signal centered at 7.59 ppm is found in the spectrum of **2**, which integrates for two hydrogens and has been assigned to the olefinic hydrogens. The FTIR spectra of **1** and **2** show the characteristic broad band between 3500 and 2500 cm^{-1} of carboxylic acid compounds. Final evidence of the structure of SiPcs **1** and **2** was given by HR-MALDI-TOF mass spectrometry where molecular ion peaks at 870.1605 and 972.1895 are in accordance with the expected values.

Optical and electrochemical measurements

The UV-vis absorption spectrum of SiPc **2** in DMF is displayed in Fig. 2. The sharp and intense well-defined Q-band centered at 687 nm indicates the lack of aggregation phenomena in solution. This behavior is quite important for an effective sensitization of the dye [11]. The spectrum for SiPc **1** is quite similar, being the Q-band maximum at 686 nm . The steady state fluorescence spectra of phthalocyanines **1** and **2** were also measured in DMF ($\lambda_{\text{exc}} = 686\text{ nm}$). From the intersection of the normalized absorption and emission spectra, the zero-zero excitation energy (E_{0-0}) can be determined [12]. As far as emission and absorption spectra are quite similar for

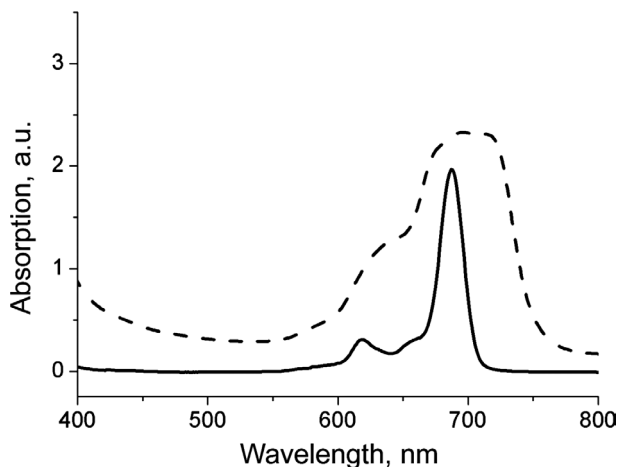


Fig. 2. UV-vis absorption spectra of SiPc **2** in solution (full line, $\times 10^{-5}\text{ M}$, DMF) and adsorbed onto TiO_2 surface (dashed line)

both SiPc **1** and **2**, a unique value of 1.79 eV for E_{0-0} is inferred from spectroscopic measurements. As expected, SiPc **3**, shows quite similar UV-vis and fluorescence spectra than those reported for **1** and **2**. This fact shows that axial substitution has a small or negligible

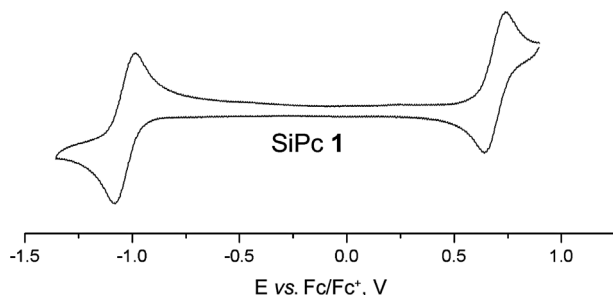


Fig. 3. Cyclic voltammogram ($100 \text{ mV}\cdot\text{s}^{-1}$) of $\sim 0.5 \text{ mM}$ SiPc **1**. Freshly distilled THF containing 0.10 M of TBAPF₆ was used as supporting electrolyte

effect on the spectroscopic properties of SiPcs. On the other hand, the solid-state spectrum of SiPcs **1** and **2** adsorbed onto titania shows a broadening of the phthalocyanine Q-band. This enlargement is mainly due to the adsorption of the dye molecules onto the transparent mesoporous TiO₂ (Fig. 2).

The electrochemical characterization of SiPcs **1** and **2** was performed using cyclic voltammetry in THF as solvent containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte (Fig. 3). One oxidation and one reduction, both quasireversible one-electron waves, can be distinguished for both SiPcs **1** and **2** which are centered at $E_{\text{ox}} = 0.69 \text{ V}$ (vs. Fc/Fc⁺) and $E_{\text{red}} = -1.03 \text{ V}$ (vs. Fc/Fc⁺), respectively. The electrochemically calculated HOMO–LUMO gap ($E_{\text{ox}} - E_{\text{red}}$), 1.72 eV , is in agreement with the E_{0-0} energy, previously obtained from spectroscopic measurements.

The electrochemical characterization allows to determine the energy of the HOMO orbital [13] (Table 1) and, together with the 0–0 transition energy, the energy of the LUMO orbital can be calculated using the equation:

$$E_{\text{LUMO}} (\text{eV}) = E_{\text{HOMO}} - E_{0-0} \quad (1)$$

All the optical and redox parameters of SiPcs **1** and **2** are listed in Table 1.

Taking into account these values, together with the energy value for the conduction band of TiO₂ ($\sim -4.2 \text{ eV}$) [14] and the energy level of the I[−]/I₃[−] redox couple (-4.89 eV) [15], an energy level diagram can be sketched and driving forces for electron injection and regeneration processes evaluated (Fig. 4). The LUMO positions for SiPcs **1** and **2** are higher than TiO₂ conduction band,

which is a fundamental requisite in order to make the electron injection from the excited dye to the TiO₂ electrode thermodynamically feasible. Moreover, HOMO levels are lower than the energy level of I[−]/I₃[−] redox couple, enabling the regeneration of the oxidized dye.

Photovoltaic and photoelectrochemical properties of phthalocyanine-sensitized TiO₂ cells

The DSC devices made from SiPcs **1** and **2** were characterized by j – V curves (Fig. 5) and the resulting photovoltaic parameters are summarized in Table 2. It is clearly observed that the device made with SiPc **2** gives higher open circuit voltage (V_{oc}) and also higher injection (j_{sc}), so the overall conversion efficiency is larger than for SiPc **1**. Comparing these results with those of a N719 DSC with the same electrolyte composition, it is clearly observed that the injection in the latter is larger, probably due to the highest light absorption from the solar spectra [5d] and the thicker titania film used (so the amount of dye attached to the TiO₂ is higher). The V_{oc} (with the same electrolyte composition) is also higher for the Ru-DSC, which is attributed to a lower electron back recombination [16].

Taking into account the fact that the HOMO–LUMO levels and the UV-vis absorption spectra (Figs 4 and 2) for both SiPcs **1** and **2** are quite similar, the better results in the DSC performance for SiPc **2** may be attributed to the different acceptor group in the dye. In the case of SiPc **2**, the presence of an additional nitrile group close to the anchoring carboxylic acid group acts as an electron withdrawing (pull) group, increasing the injection efficiency [17] and improving the performance of the photovoltaic device.

EXPERIMENTAL

General methods

All chemicals were reagent-grade, purchased from commercial sources, and used as received, unless otherwise specified. Column chromatography was performed on silica gel 60ACC 40–63 μm . Thin layer chromatography was carried out on TLC plates coated with SiO₂ (40–63 μm) 60F254, and they were visualized by UV

Table 1.

Compound	$\lambda (\text{abs})_{\text{max}}^{\text{a}}$, nm (log ϵ , M ^{−1} ·cm ^{−1})	$\lambda (\text{em})_{\text{max}}^{\text{a}}$, nm	E_{ox}^{b} (V vs. Fc/Fc ⁺)	$E_{\text{red}}^{\text{b}}$ (V vs. Fc/Fc ⁺)	E_{0-0}^{c} , eV	$E_{\text{HOMO}}^{\text{d}}$, eV	$E_{\text{LUMO}}^{\text{e}}$, eV
SiPc 1	686 (5.31)	694	0.69	−1.03	1.79	−5.49	−3.70
SiPc 2	687 (5.29)	696	0.69	−1.03	1.79	−5.49	−3.70

^a Absorption and emission spectra were measured in DMF. ^b Redox potentials were measured in THF with 0.1 M TBAPF₆ vs. Fc/Fc⁺. ^c E_{0-0} (eV) was determined from intersection of normalized absorption and emission spectra registered in DMF. ^d E_{HOMO} was calculated by $E_{\text{HOMO}} (\text{eV}) = -E_{\text{ox}} (\text{vs. Fc/Fc}^+) - 4.8$. ^e E_{LUMO} was calculated by $E_{\text{LUMO}} (\text{eV}) = E_{\text{HOMO}} (\text{eV}) + E_{0-0} (\text{eV})$.

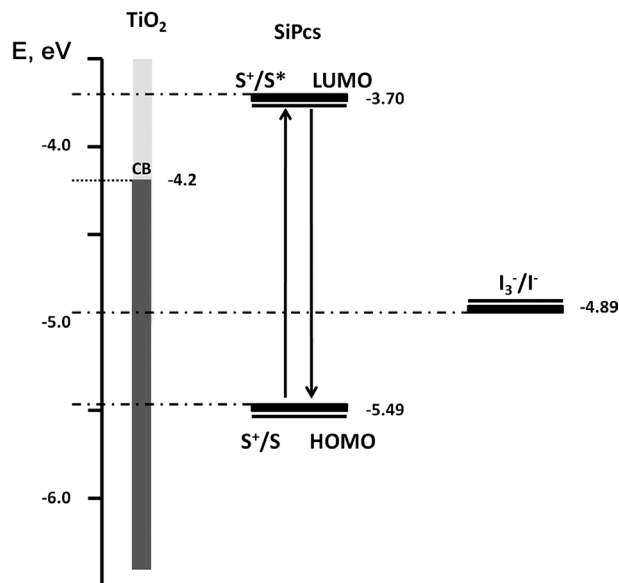


Fig. 4. Energy level diagram sketched from spectral and electrochemical data

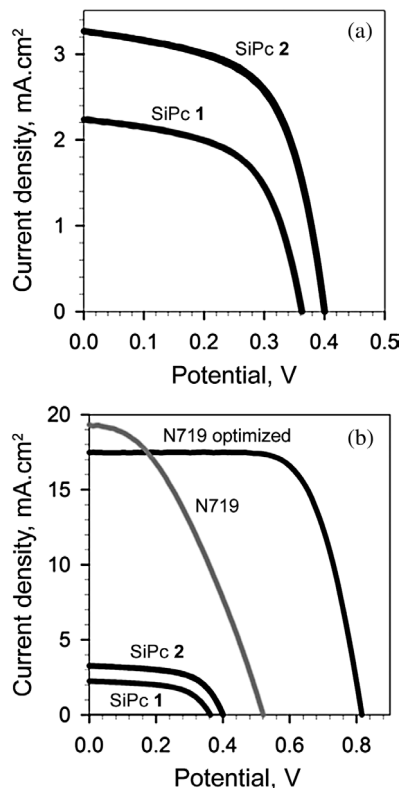


Fig. 5. (a) Current-voltage curves measured for DSCs based on SiPcs 1 and 2 as photosensitizers, under AM 1.5 G simulated sunlight. (b) compared current-voltage curves with N719 dye

Table 2. Values of V_{oc} , j_{sc} , FF and efficiency (η) obtained at steady state measurement under 100 mW.cm^{-2} light intensity and AM 1.5 global radiation

Compound	V_{oc} , V	j_{sc} , mA.cm^{-2}	FF	η , %
SiPc 1	0.34	2.25	0.69	0.53
SiPc 2	0.40	3.26	0.59	0.77

light. NMR spectra were measured with a Bruker AC 300. UV-vis spectra were recorded with a Helios Gamma spectrophotometer. Fluorescence spectra were recorded with a Perkin Elmer LS 55 Luminiscence Spectrometer and IR spectra with a Nicolet Impact 400D spectrophotometer. High Resolution Mass spectra were obtained from a Bruker Reflex III matrix-assisted laser desorption/ionization time of flight (MALDI-TOF).

Electrochemical measurements

CV measurements were performed in a conventional three-electrode cell using a μ -AUTOLAB type III potentiostat/galvanostat at 298 K, over freshly distilled THF and deaerated sample solutions ($\sim 0.5 \text{ mM}$), containing 0.10 M tetrabutylammonium hexafluorophosphate (TBAPF_6) as supporting electrolyte. A glassy carbon (GC) working electrode, Ag/AgNO_3 reference electrode and a platinum wire counter electrode were employed. Ferrocene/ferrocenium was used as an internal standard for all measurements.

Fabrication and characterization of DSCs

The DSC devices were fabricated according to a sandwich-type structure. On the working electrodes [Transparent Conducting Oxide (TCO) glass, Pilkington TEC15, $\sim 15 \text{ }\Omega/\text{sq}$ resistance] was previously deposited a compact layer of TiO_2 ($\sim 100 \text{ nm}$) by spray pyrolysis in order to avoid the possible electron/electrolyte recombination reaction at the SnO_2 surface [18]. Then, the layers of TiO_2 nanoparticles were deposited on using the Doctor Blade technique. The resulting photo-electrodes of $8\text{--}9 \text{ }\mu\text{m}$ thickness were sintered at $450 \text{ }^\circ\text{C}$ and then immersed in 0.04 M TiCl_4 solution for 30 min at $70 \text{ }^\circ\text{C}$ followed by calcination at $570 \text{ }^\circ\text{C}$ for 30 min to obtain good electrical contact between the nanoparticles. When the temperature decreased until $40 \text{ }^\circ\text{C}$ all the electrodes were immersed into the dye solutions overnight (0.5 mM in DMF). After the adsorption of the dye on TiO_2 films, the working electrodes were rinsed with the same solvent used for dye solution. The DSC devices were assembled with counter electrode (thermally platinumized TCO) using a thermoplastic frame (Surlyn $25 \text{ }\mu\text{m}$ thick). Redox electrolyte [lithium iodide (LiI , 0.5 M), diiodine (I_2 , 0.05 M) in methoxypropionitrile] was introduced through a hole drilled in the counter electrode that was sealed later.

In order to compare both Pcs with a commercial ruthenium dye, two cells based on N719 dye were fabricated (named N719 and N719 optimized). The preparation was carried out under the same conditions, but using $17 \text{ }\mu\text{m}$ thickness of TiO_2 film, due to the lower molar extinction coefficient of the Ru dye. The electrolyte composition for the N719 optimized solar cell was 0.6 M 1-methyl-3-propylimidazolium iodide, 0.03 M I_2 , 0.5 M 4-*tert*-butylpyridine, 0.1 M guanidinium thiocyanate in acetonitrile/valeronitrile ($85:15 \text{ v:v}$).

Prepared solar cells (0.5 cm² size, masking solar cell to 0.25 cm²) were characterized by current density-voltage (*j*-*V*) characteristics. Photocurrents and voltages were measured using a solar simulator equipped with a 1000 W ozone-free Xenon lamp and AM 1.5 G filter (Oriel), and the light intensity was adjusted according to an NREL-calibrated Si solar cell with a KG-5 filter to one-sun.

Synthesis

Preparation of silicon phthalocyanine 3. A mixture of silicon(IV) phthalocyanine dichloride (300 mg, 0.49 mmol) and 4-formylbenzoic acid (735 mg, 4.90 mmol) in diglyme (6 mL) was heated at reflux under argon atmosphere during 5 h. After cooling, the reaction mixture was precipitated in water, and the resulting green powder was dissolved in hot CHCl₃ (200 mL). The organic solution was filtered prior to be washed with sodium bicarbonate solution, water and brine. The pure product was obtained as a blue-green solid (143 mg, 35%) after complete evaporation of the solvent under reduced pressure. HR-MS (MALDI-TOF, DCTB): *m/z* [M]⁺ calcd. for C₄₈H₂₆N₈O₆Si 838.1739; found 838.1798. ¹H NMR (300 MHz; 25 °C; CDCl₃): δ, ppm 5.25 (4H, d, *J* = 8.6 Hz, Ar-H), 6.76 (4H, d, *J* = 8.6 Hz, Ar-H), 8.44–8.40 (8H, m, Pc-Ar-H), 9.39 (2H, s, CHO), 9.76–9.71 (8H, m, Pc-Ar-H). UV-vis (DMF): λ_{max}, nm (log ε) 360 (4.87), 619 (4.57), 658 (4.51), 688 (5.35). FT-IR (KBr): ν, cm⁻¹ 3058, 3020, 1706, 1686, 1530, 1432, 1338, 1199, 1125, 1084.

Preparation of silicon phthalocyanine 1. Silicon(IV) phthalocyanine 3 (50 mg, 0.060 mmol), sulfamic acid (H₃NO₃S, 40 mg, 0.412 mmol) and sodium chlorite (30 mg, 0.265 mmol) in a 6:1 THF/H₂O mixture (10 mL) were stirred at room temperature for 12 h. The crude product was precipitated in water, filtered and redissolved in THF. The resulting organic solution was dried over anhydrous Na₂SO₄ and the pure product was obtained as a blue-green solid (45 mg, 85%) after the complete evaporation of solvent under reduced pressure. HR-MS (MALDI-TOF, DCTB): *m/z* [M]⁺ calcd. for C₄₈H₂₆N₈O₈Si 870.1637; found 870.1605. ¹H NMR (300 MHz; 45 °C; DMSO-*d*₆): δ, ppm 5.06 (4H, d, *J* = 8.3 Hz, Ar-H), 6.83 (4H, d, *J* = 8.3 Hz, Ar-H), 8.69–8.50 (8H, m, Pc-Ar-H), 9.82–9.68 (8H, m, Pc-Ar-H). UV-vis (DMF): λ_{max}, nm (log ε) 361 (4.79), 618 (4.50), 657 (4.44), 686 (5.31). FT-IR (KBr): ν, cm⁻¹ 3650–2353, 1726, 1689, 1530, 1432, 1338, 1292, 1125, 1084.

Preparation of silicon phthalocyanine 2. A mixture of silicon(IV) phthalocyanine 3 (50 mg, 0.060 mmol), cyanoacetic acid (30 mg, 0.352 mmol) and piperidine (40 μL, 0.404 mmol) in dry DMF (5 mL) was stirred at 100 °C under argon atmosphere during 3 h. After cooling, the crude product was precipitated in HCl 0.5 M, filtered and washed with water and methanol. The pure product was obtained as a blue green powder (30 mg, 50%) after repetitive dichloromethane washes. HR-MS (MALDI-

TOF, dithranol): *m/z* [M]⁺ calcd. for C₅₄H₂₈N₁₀O₈Si 972.1866; found 972.1895. ¹H NMR (300 MHz; 45 °C; DMSO-*d*₆): δ, ppm 5.11 (4H, d, *J* = 8.3 Hz, Ar-H), 6.88 (4H, d, *J* = 8.3 Hz, Ar-H), 7.59 (2H, br s, Ar-CH=), 8.65–8.51 (8H, m, Pc-Ar-H), 9.83–9.69 (8H, m, Pc-Ar-H). UV-vis (DMF): λ_{max}, nm (log ε) 361 (4.80), 619 (4.49), 687 (5.29). FT-IR (KBr): ν, cm⁻¹ 3690–2304, 2224, 1720, 1686, 1610, 1530, 1432, 1338, 1292, 1125, 1084.

CONCLUSION

Two new silicon phthalocyanines (SiPcs) axially substituted with carboxylic acid appends have been synthesized and chemically characterized. Although similar HOMO–LUMO values are obtained for both SiPcs, the device made with SiPc 2 gives higher open circuit voltage (*V*_{oc}) and also higher injection (*j*_{sc}), so the overall conversion efficiency is larger than that of the device based on SiPc 1. The presence of an additional nitrile group close to the anchoring carboxylic acid group, which acts as an electron withdrawing (pull) group, increases the injection efficiency and improves the performance of the photovoltaic device.

The results we obtained are fairly promising and should encourage further studies on DSCs using axially anchored SiPc derivatives substituted with withdrawing groups.

Acknowledgements

We thank financial support from Ministerio de Ciencia e Innovación under projects HOPE CSD2007-00007, CTQ2008-05901/BQU, CTQ2010-20349, MAT2010-19827 and PLE2009-0042, and Generalitat Valenciana under project PROMETEO/2009/058.

REFERENCES

- O'Reagan B and Grätzell M. *Nature* 1991; **353**: 737–740.
- a) Chen BS, Chen YJ and Chou PT. *J. Mater. Chem.* 2011; **21**: 4090–4094. b) Xu F, Dai M, Lu Y and Sun L. *J. Phys. Chem. C* 2010; **114**: 2776–2782. c) Raja S, Satheeshkumar C, Rajakumar P, Ganesan S and Maruthamuthu P. *J. Mater. Chem.* 2011; **21**: 7700–7704. d) Lin LY, Tsai CH, Wong KT, Huang TW, Wu CC, Chou SH, Lin F, Chen SH and Tsai AI. *J. Mater. Chem.* 2011; **21**: 5950–5958. e) Shalom M, Alberio J, Tachan Z, Martínez-Ferrero E, Zaban A and Palomares E. *J. Phys. Chem. Lett.* 2010; **1**: 1134–1138. f) Mikroyannidis JA, Kabanakis A, Balraju P and Sharma GD. *J. Phys. Chem. Lett. C* 2010; **114**: 12355–12363. g) Odobel F, Le Pleux L, Pellegrin Y and Blart E. *Acc. Chem. Res.* 2010; **43**: 1063–1071. h) Kolemen S, Bozdemir OA, Cakmak Y, Barin G, Erten-Ela S, Marszalek M, Yum JH, Zakeeruddin SM, Nazeeruddin MK, Grätzel M and Akkaya EU. *Chem. Sci.* 2011; **2**: 949–954. i) Cai N,

- Moon SJ, Cevey-Ha L, Moehl T, Humphry-Baker R, Wang P, Zakeeruddin SM and Grätzel M. *Nano Lett.* 2011; **11**: 1452–1456.
3. a) Nazeeruddin MK, Péchy P, Renouard T, Zakeeruddin SM, Humphry-Baker R, Comte P, Liska P, Cevey L, Costa E, Shklover V, Spiccia L, Deacon GB, Bignozzi CA and Grätzel M. *J. Am. Chem. Soc.* 2001; **123**: 1613–1624. b) Nazeeruddin MK, De Angelis F, Fantacci S, Selloni A, Viscardi G, Liska P, Ito S, Takeru B and Grätzel M. *J. Am. Chem. Soc.* 2005; **127**: 1635–1647. c) Gao F, Wang Y, Shi D, Zhang J, Wang M, Jing X, Humphry-Baker R, Wang P, Zakeeruddin S and Grätzel M. *J. Am. Chem. Soc.* 2008; **130**: 10720–10728. d) Chen C, Wang M, Li J, Pootrakulchote N, Alibabaei L, Ngocle C, Decoppet JD, Tsai JH, Grätzel C, Wu CG, Zakeeruddin SM and Grätzel M. *ACS Nano* 2009; **3**: 3103–3109.
 4. a) Imahori H, Uemeyama T and Seigo IT. *Acc. Chem. Res.* 2009; **42**: 1809–1818. b) Walter MG, Rudine AB and Wamser CC. *J. Porphyrins Phthalocyanines* 2010; **14**: 759–792. c) Bessho T, Zakeeruddin SM, Yeh CYu, Diao EWG and Grätzel M. *Angew. Chem. Int. Ed.* 2010; **49**: 6646–6649.
 5. a) Mori S, Nagata M, Nakahata Y, Yasuta K, Goto R, Kimura M and Taya M. *J. Am. Chem. Soc.* 2010; **132**: 4054–4055. b) Martínez-Díaz MV, de la Torre G and Torres T. *Chem. Commun.* 2010; **46**: 7090–7108. c) Bottari G, de la Torre G, Guldi DM and Torres T. *Chem. Rev.* 2010; **110**: 6768–6816. d) Barea EM, Ortiz J, Payá FJ, Fernández-Lázaro F, Fabregat-Santiago F, Sastre-Santos Á and Bisquert J. *Energy Environ. Sci.* 2010; **3**: 1985–1994. e) García-Iglesias M, Cid JJ, Yum JH, Humphry-Baker R, Zakeeruddin SM, Péchy P, Vázquez P, Palomares E, Grätzel M, Nazeeruddin MK and Torres T. *Chem. Sci.* 2011; **2**: 1145–1150.
 6. a) Palomares E, Martínez-Díaz MV, Haque SA, Torres T and Durrant JR. *Chem. Commun.* 2004; 2112–2113. b) Morandeira A, Lopez-Duarte I, Martínez-Díaz MV, O'Regan BC, Shuttle C, Haji-Zainulabidin NA, Torres T, Palomares E and Durrant JR. *J. Am. Chem. Soc.* 2007; **129**: 9250–9251. c) Atilla D, Saydan N, Durmuş M, Gürek AG, Khan T, Rück A, Walt H, Nyokong T and Ahsen V. *J. Photochem. Photobiol. A* 2007; **186**: 298–307.
 7. a) Cheng G, Peng X, Hao G, Kennedy VO, Ivanov IN, Knappenberger K, Hill TJ, Rodgers MAJ and Kenney ME. *J. Phys. Chem. A* 2003; **107**: 3503–3514. b) Rodríguez-Redondo JL, Sastre-Santos Á, Fernández-Lázaro F, Soares D, Azzellini GC, Elliot B and Echegoyen L. *Chem. Commun.* 2006: 1265–1267. c) Martín-Gomis L, Ohkubo K, Fernández-Lázaro F, Fukuzumi S and Sastre-Santos Á. *Org. Lett.* 2007; **9**: 3441–3444. d) Martín-Gomis L, Ohkubo K, Fernández-Lázaro F, Fukuzumi S and Sastre-Santos Á. *J. Phys. Chem. C* 2008; **112**: 17694–17701. e) Martín-Gomis L, Ohkubo K, Fernández-Lázaro F, Fukuzumi S and Sastre-Santos Á. *Chem. Commun.* 2010; **46**: 3944–3946. f) Céspedes-Guirao FJ, Martín-Gomis L, Ohkubo K, Fukuzumi S, Fernández-Lázaro F and Sastre-Santos Á. *Chem. Eur. J.* 2011; **17**: 9153–9163.
 8. a) Honda S, Nogami T, Ohkita H, Bente H and Ito S. *ACS Appl. Mater. Interfaces* 2009; **4**: 804–810. b) Honda S, Yokoya S, Ohkita H, Bente H and Ito S. *J. Phys. Chem. C* 2011; **115**: 1306–1317.
 9. Honda S, Yokoya S, Ohkita H, Bente H and Ito S. *Chem. Commun.* 2010; **46**: 6596–6598.
 10. Macor L, Fungo F, Tempesti T, Durantini EN, Otero L, Barea EM, Fabregat-Santiago F and Bisquert J. *Energy Environ. Sci.* 2009; **2**: 529–534.
 11. Palomares E, Martínez-Díaz MV, Haque SA, Torres T and Durrant JR. *Chem. Commun.* 2004: 2112–2113.
 12. Gierschner J, Cornil J and Egelhaaf HJ. *Adv. Mater.* 2007; **19**: 173–191.
 13. E_{HOMO} (eV) = -4.8 - E_{ox} V (vs. Fc/Fc⁺).
 14. Grätzel M. *Nature* 2001; **414**: 338–344.
 15. a) Eu S, Katoh T, Uemeyama T, Matano Y and Imahori H. *Dalton Trans.* 2008: 5476–5483. b) Pablichuk VV and Addison AW. *Inorg. Chim. Acta* 2000; **298**: 97–102.
 16. Caballero R, Barea EM, Fabregat-Santiago F, de la Cruz P, Márquez L, Langa F and Bisquert J. *J. Phys. Chem. C* 2008; **12**: 18623–18627.
 17. Reddy PY, Giribabu L, Lyness C, Snaith HJ, Vijaykumar C, Chandrasekharan M, Lakshmikantham M, Yum JH, Kalyanasundaram K, Grätzel M and Nazeeruddin MK. *Angew. Chem. Int. Ed.* 2007; **46**: 373–376.
 18. O'Regan BC, Lopez-Duarte I, Martínez-Díaz MV, Forneli A, Albero J, Morandeira A, Palomares E, Torres T and Durrant JR. *J. Am. Chem. Soc.* 2008; **130**: 2906–2907.