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Communication

The Influence of Substituent Orientation on the Photovoltaic Performance of Phthalocyanine-Sensitized Solar Cells

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Orientation matters: Different regioisomers of a carboxy-ZnPc substituted at the non-peripheral (α) positions by rigid aryl groups have shown a distinct photovoltaic response, which has been correlated with the steric hindrance and/or orientation of the substituent around the anchoring group.

Different #regioisomers of a #phthalocyanine show a distinct #photovoltaic response

Dye-Sensitized Solar Cells

near-IR dyes

panchromatic sensitization

phthalocyanines

solar cells

substituent effect

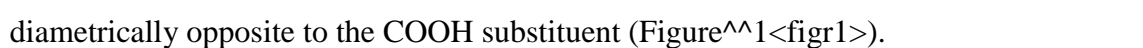
Phthalocyanines (Pcs) are used as sensitizers in dye-sensitized solar cells (DSSCs) because of their stability and intense absorption in the red and near-IR regions. Impressive progress has been made in photovoltaic efficiencies by introduction of bulky peripheral substituents to help suppress macrocycle aggregation. To reach benchmark efficiencies reported for other related dyes, new designs need to be explored. Single carboxy-ZnPc regioisomers substituted at the non-peripheral positions by rigid aryl groups have now been studied, which has shed light on the influence of steric hindrance and/or orientation of the substituent around the anchoring group on the photovoltaic response. The regioisomer bearing the aryl group far away from the anchoring group produces a more effective sensitization of the TiO₂ films and higher short-circuit photocurrent density (J_{sc}). Taking advantage of the good photovoltaic performance in the near-IR region of this ZnPc, it was combined with another appropriate dye for panchromatic sensitization of the mesoporous photoelectrode and an increase of the overall device efficiency.

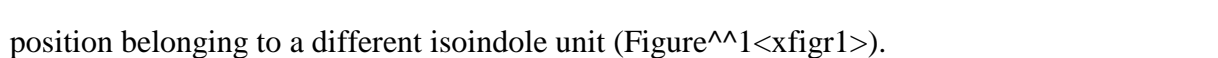
In the last 15 years, the field of porphyrin and phthalocyanine (Pc)-sensitized solar cells (DSSCs) has experienced an exponential growth, and high efficiencies over 13% have been reached based on a rational molecular design.^[1,^2] In the case of Pcs, the basic structural requirements, such as incorporation of peripheral bulky donor substituents, have been established to both minimize aggregation of the dye on the TiO₂ surface and achieve a directional excited state to facilitate efficient injection of electrons onto the semiconductor. Moreover, the stability of Pcs as photosensitizers in DSSCs is much higher than that of porphyrin analogues.^[2]

The lack of planarity exhibited by non-peripheral (or α) substituted Pcs is responsible for their reduced aggregation properties.^[3] However, this family of Pcs has not been sufficiently explored as non-aggregated dyes in Pc-DSSCs, most probably because of the discouraging results reported up to now. From the first example, PCH003,^[4] described by Giribabu et al. in 2007, which had a 1.1% overall photovoltaic power-conversion efficiency (PCE), to the most recent molecules, PcS5^[5] and Zn-Thio-Pc,^[6] with efficiencies of 2.1% and 0.4% respectively, results are far from the records achieved by peripheral (or β) substituted Pc derivatives. We have considered that this different performance between α and β substituted Pcs could be originated by the steric hindrance produced by the bulky substituents around the anchoring group. Indeed, Kimura et al. previously reported the effect of bulkiness of peripheral (or β) substituents around the carboxy group on Pc-DSSCs.^[2e] If bulky groups are pointing towards the TiO₂ surface, the anchoring of the dye to the semiconducting surface might be difficult, therefore causing a decreasing amount of dye anchored and, consequently, resulting low power conversion efficiency.

Recently, we reported nonaggregated carboxy-ZnPc **1**, with potential application in DSSCs, having bulky and rigid aryl substituents, namely 3,5-di-*tert*-butylphenyl, directly linked to three of the nonperipheral (or α) positions of the macrocycle.^[7] Furthermore, following previous examples of efficient carboxy-ZnPc dyes, a carboxylic acid moiety, which is required to graft the dye to the semiconducting TiO₂, was directly attached at the Pc core, specifically at a peripheral (or β) position.

Tetrasubstituted unsymmetrical A₃B-type Pcs are formed in a cyclotetramerization reaction as a mixture of eight regioisomers presenting different symmetries. However, in the case of ZnPc **1**, the bulkiness and rigidity of the 3,5-di-*tert*-butylphenyl substituents led us to achieve the regioselective formation of only four macrocycles, ZnPcs **1^{a-d}**, in which two aryl bulky substituents cannot be found pointing towards the same Pc corner, to avoid steric hindrance. Moreover, the appropriate balance between both the rigidity and bulkiness of the α -aryl substituents and the polarity of the β -carboxylic acid function resulted in the isolation of regioisomers **1^a** and **1^b** by standard column chromatography. Regioisomers **1^c** and

1^d eluted together since they only differ in the relative position of the aryl bulky group diametrically opposite to the COOH substituent (Figure¹.

This notable achievement gives rise to the unprecedented study, reported herein, on the use of single carboxy-ZnPc regioisomers **1^a**, **1^b** and a mixture of **1^{c/d}** as dyes in DSSCs, which can shed light on the influence of steric hindrance and/or orientation of a rigid substituent around the anchoring group in the photovoltaic response. Additionally, with the aim of making a comparison between α and β -substituted Pcs, we synthesized ZnPc **2** (Supporting Information, Scheme^{S2}) as a mixture of eight regioisomers. ZnPc **2** is an unsymmetrical A₃B-type Pc, which has 3,5-di-*tert*-butylphenyl substituents at three peripheral (or β) positions of the macrocycle and a carboxylic acid group directly attached at another β position belonging to a different isoindole unit (Figure¹.

Concerning the least planar macrocycle ZnPc **1**, regioisomers **1^c** and **1^d** have both 3,5-di-*tert*-butylphenyl groups located at 8 and 25 positions of the macrocycle, therefore, two rigid and bulky groups are pointing towards the COOH anchoring group. In regioisomer **1^b**, the bulky substituents are oriented in a clockwise direction, being the 25 position of the Pc macrocycle occupied whereas the 8 position is free. Therefore, there is only one bulky substituent close to the carboxy group. Finally, regioisomer **1^a** presents the bulky groups oriented in an anti-clockwise direction, being the 8 position of the macrocycle occupied when, in fact, the 25 position remains free. Hence, it is expected that the lowest steric hindrance around the carboxy group be in the regioisomer **1^a** since there is no substituent at 25 position, the closest to the anchoring group.

With regard to the regioisomeric mixture of ZnPc **2**, being a β -substituted macrocycle, the 8 and 25 <ga> positions are always free. In this way, none of the regioisomers has the rigid and bulky groups pointing directly towards the TiO₂ surface, therefore, steric hindrance should not be the main issue for their photovoltaic response. However, this molecule presents a higher degree of planarity than α -substituted ZnPc **1**, and may form dye aggregates onto the TiO₂ surface.

Taking all of the above data into consideration, we focused on the study of the sensitizing capabilities of the new regioisomerically pure α -triaryl- β -carboxyphthalocyanines **1^a**, **1^b**, and the mixture of **1^{c/d}**. Photoanodes consisting of 8 μm of transparent TiO_2 plus 4 μm scattering TiO_2 film (8+4) were used. After 8 h sensitization into a 0.1 mM solution of the dye in ethanol, differences in the amount of dye adsorbed by the photoanode in each of the dye solutions can be easily visualized (Supporting Information, Figure S1). UV/Vis spectroscopy of the dye adsorbed on TiO_2 nanoparticles (Figure 2) shows that ZnPc **1^a** is loaded by far in a larger amount in comparison to the loading of **1^b** and **1^{c/d}**. Consequently, it is demonstrated that the lower steric congestion around the carboxy anchoring group the larger sensitization of the TiO_2 films.

The density of the dye adsorbed on the mesoporous TiO_2 films was determined by measuring the absorbance of the phthalocyanines released from the dye-stained TiO_2 films (Supporting Information, Figure S2). The adsorption densities on the TiO_2 films were determined to be $3.9 \times 10^{-8} \text{ mol cm}^{-2}$ for regioisomer **1^a**, $2.1 \times 10^{-9} \text{ mol cm}^{-2}$ for **1^b**, and $1.2 \times 10^{-9} \text{ mol cm}^{-2}$ for **1^{c/d}**.

Therefore, the adsorption density of **1^a** is one order of magnitude higher than that of **1^b** and **1^{c/d}**. In turn, the adsorption density of **1^b** is about 1.75 times higher than that of **1^{c/d}**. When measuring the adsorption density of ZnPc **1**, which is a mixture of all the regioisomers **1^a**, **1^b**, **1^{c/d}** in 1:1:1.6 ratio, it resulted in a value of $3.0 \times 10^{-8} \text{ mol cm}^{-2}$, which is about 1.3 times smaller than that of regioisomer **1^a**. These results let demonstrate that each of the regioisomers of the α -triaryl- β -carboxyphthalocyanine **1** are adsorbed in a different quantity onto TiO_2 surface according to the steric hindrance around the anchoring carboxy group of the molecule. Specifically, regioisomer **1^a** is the only one that can be adsorbed by the photoanode in a high density.

The DSSC performance of regioisomers **1^{a--d}**, and the regioisomeric mixtures of ZnPc **1** and ZnPc **2**, was examined using 8+4 doubled-layered TiO_2 electrodes with electrolytes containing 0.86 M 1,3-dimethylimidazolium iodide, 0.2 M LiI, 0.04 M I_2 , 0.29 M

4-*tert*-butylpyridine and 0.05 M guanidine thiocyanate in acetonitrile, under standard air mass 1.5 global (AM^{1.5G}) solar irradiation.

Figure³ (top) shows the photocurrent density--voltage curves of DSSCs based on the pure regioisomer **1^a**. These devices exhibited a short-circuit photocurrent density (J_{sc}) of 8.8 mA cm⁻² at one sun and 4.5 mA cm⁻² and 0.9 mA cm⁻² under 50 mW cm⁻² and 10 mW cm⁻² solar irradiation, respectively.

Figure³ (bottom) shows the photocurrent density--voltage curves under one-sun irradiation of DSSCs prepared with pure regioisomers **1^a** and **1^b**, the mixture of **1^{c/d}**, and the mixture of the four regioisomers of ZnPc **1**. As already stated, the J_{sc} value of **1^a** is 8.8 mA cm⁻², which means the highest value achieved by any of the regioisomers or the mixture of all of them. This value is 1.2 times the J_{sc} of ZnPc **1**, which is 7.4 mA cm⁻². It is also 3.7 times the J_{sc} of **1^b**, that is 2.4 mA cm⁻², and 11 times higher than that of **1^{c/d}**, which is 0.8 mA cm⁻². These noteworthy differences among the J_{sc} values are a direct consequence of the lower adsorption densities of **1^b** and **1^{c/d}**.

Table¹ shows the short-circuit photocurrent density, open-circuit photovoltage (V_{oc}), fill factor (FF), and PCE obtained for regioisomers **1^{a--d}** and the mixture ZnPc **1** under one-sun irradiation. The **1^a** cell exhibits a V_{oc} of 577 mV, a FF of 0.73, yielding a PCE of 3.7%. The incident photon-to-electron conversion efficiency (IPCE) spectrum of the **1^a** cell followed the absorption feature of this regioisomer adsorbed on the TiO₂ electrode (Figure⁴). The IPCE at the maximum absorption of the Q band (700 nm) reaches 73%, and curve integration over the solar spectrum gives a short-circuit photocurrent of 8.9 mA cm⁻², which is in agreement with the measured device photocurrent. However, the **1^b** cell shows a V_{oc} of 533 mV, a FF of 0.73, yielding a PCE of 0.9% because of the low J_{sc} value. In this case, the maximum IPCE value was 39% at 700 nm. The **1^{c/d}** cell exhibits a V_{oc} of 512 mV, a FF of 0.71, yielding a PCE of 0.3%. This efficiency value is in consonance with the low adsorption density of these two regioisomers owing to the fact that they both present rigid and bulky groups around the anchoring carboxy group. The maximum IPCE value was 11% at 700 nm. Finally, the

regioisomeric mixture ZnPc **1** cell presents a V_{oc} of 523 mV, a FF of 0.72, yielding a PCE of 2.8%, almost 1% less than that of the **1^a** cell. The maximum IPCE value at 700 nm was a 15% less than that achieved by the **1^a** device at the same wavelength.

As previously established, the non-peripheral (or α) substituted Pcs are the least planar family in such macrocycles, and therefore they exhibit reduced aggregation properties. That is evidenced by the results of the Table² where efficiency values of devices, either prepared with the coadsorption of chenodeoxycholic acid (CDCA) or without any co-adsorbent, are compared. It is widely known that the coadsorption of CDCA can hinder the formation of dye aggregates and improve electron injection yield, and thus J_{sc} . This can also lead to a rise in photovoltage, which is attributed to the decrease of charge recombination. Nevertheless, in the present case none of this happens. The photovoltaic performance of pure regioisomer **1^a** and the mixture ZnPc **1** in the presence of CDCA decreases in comparison with the absence of it. This is related not only to the lack of molecular aggregates onto the TiO₂ surface but also to a loss of dye loaded.

Nonetheless, in consonance with the photovoltaic performance of the β -substituted ZnPc **2** in Table³, the presence of CDCA causes an enhancement in the device efficiency. Coadsorption of CDCA prevents dye aggregation, which enables intermolecular energy transfer and sequentially results in the excited-state quenching of the dye. As a result, the reduction of dye loaded onto the TiO₂ surface in the presence of CDCA causes more efficient electron injection from the excited dye to the TiO₂ conduction band, and thus in J_{sc} . These results agree with those predicted, since β -substituted ZnPc **2** is a more planar macrocycle than that of α -substituted ZnPc **1**.

Taking advantage of the best photovoltaic performance of regioisomer **1^a** in the near-IR region, we decided to use it in combination with an appropriate dye to achieve panchromatic sensitization of the mesoporous photoelectrode and increase the device efficiency. Nevertheless, mixing two dyes usually results in a decrease of efficiency, which is probably due to the decreased injection efficiency caused by molecular interactions between the two dyes. Hence, prevention of electronic interactions between the dyes on the

semiconductor surface is important for the development of efficient cocktail-type DSSCs. For this reason, there are few cases reported so far in the literature in which molecular cosensitization using phthalocyanines resulted in higher efficiency values than those of single-dye devices.^[2a,8] In our case, the secondary dye chosen to complement the absorption spectrum of **1^a** in the UV/Vis region is the previously reported organic dye D35 based on triphenylamine moiety (Supporting Information, Figure^{S8}).^[9] In particular, D35 exhibits an efficiency value of 5.07% with a redox couple I^{M-}/I_3^{M-} as electrolyte, which indicates that the combination of regioisomer **1^a** and D35 resulted in higher efficiency value than that of the DSSCs using each dye separately (Table²). Specifically, the photovoltaic performance of the cocktail-type **1^a/D35** cell showed 56% increase in the J_{sc} value compared to that of the **1^a** cell. Furthermore, the V_{oc} value of the cocktail-type cell was slightly increased. The IPCE spectrum (Figure⁵) of the **1^a/D35** cell was the sum of the IPCE response for each of the dyes. The IPCE values at the near-IR region (76% at 700 nm) did not decrease by the co-sensitization, thus indicating that ZnPc **1^a** does not interact with the organic dye on the TiO₂ surface. The IPCE values at the visible region (73% at 480 nm) did not decrease either, suggesting that there is no effect on the injection efficiency of the organic dye by the co-sensitization. Presumably, the bulky and rigid substituents at the α positions of the macrocycle in **1^a** not only avoid the aggregation among the Pc dyes but also prevent the interaction with other dyes.

By comparing for the first time the photovoltaic responses in DSSCs of α and β -substituted carboxy-ZnPcs bearing at different macrocycle positions the same bulky aryl group, it can be inferred that β derivatives are considerable more prompt towards aggregation onto TiO₂ than α -substituted ZnPcs. Consequently, as mixture of regioisomers and in the absence of CDCA ZnPc **2** exhibits a lower PCE value than ZnPc **1**. This result proves that α -substituted carboxy-ZnPcs are suitable non-aggregated dyes, which are not sufficiently explored yet in DSSCs. However, in this family of α -substituted Pcs, the main issue to control is the orientation of the bulky and rigid substituent around the anchoring group, which is remarkably different in each regioisomer **1^a**, **1^b** and **1^{c/d}**. It has been

demonstrated a clear negative steric influence of the 3,5-di-*tert*-butylphenyl substituents around the carboxy group in the case of regioisomers **1^ab** and **1^ac/d**, making difficult the anchoring to the TiO₂, which causes a low loading of dye and *J*_{sc} value.

In conclusion, we have demonstrated for the first time the influence of the substituent orientation on the photovoltaic performance of β-carboxy-zinc phthalocyanines. The regioisomerically pure ZnPc **1^aa** has shown the best photovoltaic performance since it is a non-aggregated dye with a suitable substitution pattern of the bulky substituents around the anchoring group. In the same line, ZnPc **1^aa** has proven to be a good candidate for the development of efficient panchromatic cocktail-dyes for DSSCs.

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Figure¹ Structures of the regioisomers **1^a--d** of carboxy-ZnPc **1** and ZnPc **2**.

Figure² UV/Vis spectra of regioisomers **1^a--d** and the mixture of all of them (ZnPc **1**) adsorbed on the TiO₂ films.

Figure³ Photocurrent density-voltage (*J*--*V*) curves for DSSCs prepared with dye **1^a** at several light intensities (top). *J*--*V* curves for DSSCs based on regioisomers **1^a--d** and ZnPc **1** at one sun (bottom).

Figure⁴ Incident photon-to-electron conversion efficiency of the photovoltaic devices sensitized with regioisomers **1^{a-d}** and ZnPc **1**.

Figure⁵ IPCE spectrum (inset) and *J*-*V* curve of a **1^a/D35** DSSC under one-sun irradiation.

Table¹ Photovoltaic performance of DSSCs based on ZnPc **1** and regioisomers **1^{a-d}** under one-sun irradiation (100 mW cm^{-2}).

Dye	Adsorption density [mol cm ⁻²]	V _{oc} [mV]	J _{sc} [mA cm ⁻²]	FF	PCE [%]
1^a	3.9×10 ⁻⁸	577	8.8	0.73	3.7
1^b	2.1×10 ⁻⁹	533	2.4	0.73	0.9
1^{c/d}	1.2×10 ⁻⁹	512	0.8	0.71	0.3
ZnPc 1	3.0×10 ⁻⁸	523	7.4	0.72	2.8
TT1 ^[a]	--	506	6.2	0.64	2.0

[a]^aAs a reference dye, TT1 was measured using the same conditions.

Table² Photovoltaic performance of DSSCs based on ZnPc **1** and regioisomers **1^a**, with and without co-adsorbent, under one-sun irradiation (100 mW cm^{-2}).

Dye	Co-adsorbent ^[a]	V _{oc} [mV]	J _{sc} [mA cm ⁻²]	FF	PCE [%]
1^a	--	577	8.8	0.73	3.7
	CDCA	546	7.6	0.72	3.0
	D35	584	15.6	0.69	6.3

ZnPc 1	--	523	7.4	0.72	2.8
	CDCA	495	5.0	0.70	1.7

[a]^{0.05}mm of co-adsorbent is added in the ethanolic dye solution.

Table³ Photovoltaic performance of DSSCs based on ZnPc 2, with and without CDCA as co-adsorbent, under one-sun irradiation (100^{mW}cm⁻²).

Dye	CDCA [mM]^[a]	V_{oc} [mV]	J_{sc} [mA^{cm}-2]	FF	PCE [%]
2	--	523	5.5	0.72	2.1
	10	490	6.6	0.75	2.4
	30	514	7.0	0.74	2.7

[a]^{CDCA} is added in the dye solution as co-adsorbent.
