Convergent Strategy for the Regioselective Synthesis of Nonaggregated α-Triaryl-β-carboxy Zinc Phthalocyanines

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S *Supporting Information*

ABSTRACT: A new design of nonaggregated zinc(II) carboxyphthalocyanines with potential application in dye-sensitized solar cells has been developed. It is based on the introduction of bulky and rigid aryl groups at three α positions of the macrocycle. The synthesis has been carried out following a convergent route in which the bulky aryl groups are introduced by a Suzuki−Miyaura cross-coupling reaction on a preformed triiodophthalocyanine derivative. Two regioisomers of this α-triaryl-β-carboxyphthalocyanine could be isolated by column chromatography.
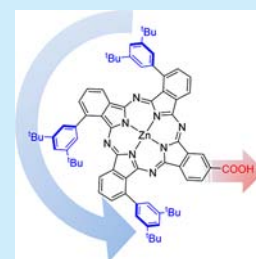
Phthalocyanines (Pcs)[1] are one of the most common electro- and photoactive components of organic solar cells because of their robustness and peculiar intense absorption in the red and near-IR spectral regions. In particular, many zinc phthalocyanines have been prepared and tested as light harvesters for dye-sensitized solar cells (DSSCs). However, conversion efficiencies are still lower than those of related porphyrins, which are the most effective organic molecules in this area.[2]

Previous work on zinc phthalocyanines has shown that control over the formation of molecular aggregates onto the semiconductor nanoparticles, namely the TiO₂, was key to achieve good efficiencies by preventing nonradiative deactivation of the dye in the excited state.[3] The first successful attempt to overcome this problem came in 2007 by preparing unsymmetrical substituted ZnPcs bearing three bulky electron-donating *tert*-butyl groups attached to peripheral (or β) positions of the macrocycle, whereas the fourth isoindole unit was functionalized with an anchoring carboxylic group.[4] The particular success of the ZnPc named **TT1** and its derivatives[5] was explained by effective suppression of aggregation of the macrocycle on the titanium dioxide surface and adequate directionality of the excited state, which facilitates an efficient electron injection. Nevertheless, **TT1** and derivatives were always prepared and studied as mixtures of eight regioisomers.

A further step was carried out from 2010[6] by incorporation of six very bulky 2,6-diphenylphenoxy groups at peripheral sites of a carboxyZnPc. Structural modifications at the peripheral aryloxy groups and variations on the linker between the Pc and the anchoring group have recently been reported, giving rise to many new nonaggregated carboxyZnPcs derivatives which have reached excellent efficiency values close to 6.5%.[7] One of the advantages of this design builds on the molecular substitution pattern that leads to monoisomeric Pc compounds. However, highly elaborated substituents would need to be prepared to further optimize the performance of Pcs in this field.

Here, we describe a novel family of nonaggregated zinc(II) carboxyphthalocyanines with potential application in DSSCs based on the introduction of simple bulky and rigid aryl substituents directly linked to the nonperipheral (or α) positions of the macrocycle. This substitution pattern will both help to suppress aggregation and allow study of the influence of substituent orientation around the anchoring group in the photovoltaic response, since pure regioisomers are isolated. Moreover, a convergent synthetic strategy has been used, which in turn resulted in an effective selective method with no precedent in Pc chemistry.

As a model molecule, phthalocyanine **1** has been designed to incorporate bulky 3,5-di-*tert*-butylphenyl substituents at three α positions of the macrocycle, whereas a carboxylic acid functional group is located as the substituent at the β position of the fourth isoindole unit of the Pc (Figure 1) as the anchoring group.

Ranta et al. have reported the regioselective preparation of the C_{4h} isomer of tetrakis(3,5-di-*tert*-butylphenyl)phthalocyanine by macrocyclization of the corresponding 3-aryl-substituted phthalonitrile,[8] demonstrating an effective steric control of the 3,5-di-*tert*-butylphenyl substituent, which restricts the formation of other possible regioisomers in which the aryl groups should be pointing toward the same Pc corner. In addition, single regioisomers of unsymmetrical A₃B-type 1,8,15,22-substituted phthalocyanines have been selectively prepared by mixed macrocyclization of two different 3-aryl-substituted phthalonitriles bearing adequate sterically restricting aryl substituents. These results indicated that our designed α-triaryl-β-carboxy ZnPc **1** could be selectively prepared as a mixture of only four (shown in Figure 1) of the eight theoretically possible regioisomers. To our knowledge, the
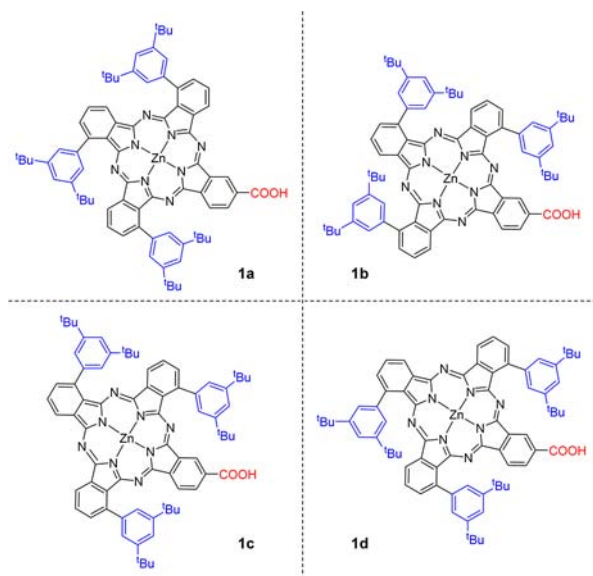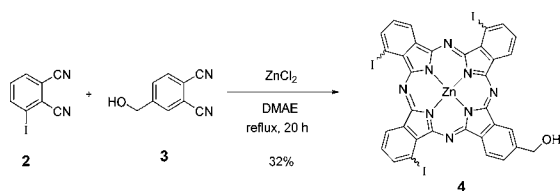
Figure 1. Possible regioisomers of the α-triaryl-β-carboxy ZnPc **1**.

regioselective preparation of A₃B-type Pcs with this substitution pattern has never been reported.

Indeed, when a 4:1 molar mixture of the bulky α-substituted 3-(3,5-di-*tert*-butylphenyl)phthalonitrile and the β-substituted 4-hydroxymethylphthalonitrile (**3**) was reacted using the conditions reported by Ranta et al.,[8] a mixture of the four possible regioisomeric Pcs was formed in low yield (ca. 5%, see the experimental details in the Supporting Information). Taking into account the large amount of starting 3-(3,5-di-*tert*-butylphenyl)phthalonitrile that had to be prepared, we decided to explore another synthetic strategy that would allow preparation of our Pc target in higher yield.

Considering our previous experience on the functionalization of β-substituted iodoZnPcs by Pd-mediated reactions, we planned the preparation of target ZnPc **1** by a convergent synthetic strategy.[9] Thus, a 4:1 molar ratio mixture of 3-iodophthalonitrile (**2**)[10] and 4-hydroxymethylphthalonitrile (**3**)[11] was reacted at reflux in DMAE in the presence of ZnCl₂. The desired A₃B ZnPc **4** was obtained in 32% yield after isolation by column chromatography (Scheme 1). At this point,

Scheme 1. Cyclotetramerization Reaction of Phthalonitriles 2 and 3

the eight possible regioisomers of Pc **4** were formed in equal amounts, as inferred from the ¹H NMR spectrum of the compound (see signals at ca. 5.2 ppm in Figure S2, Supporting Information) whose separation by column chromatography was not feasible. In conclusion, the iodine substituents at the α-position are not bulky enough for controlling the selective formation of regioisomeric Pcs.

ZnPc **4** was then oxidized with the periodinane derivative IBX (1-hydroxy-1,2-benziodoxol-3(1*H*)-one 1-oxide) in DMSO to yield the formyl derivative ZnPc **5** in 98% yield (Scheme 2).

Scheme 2. (a) Convergent Synthesis of α-Triaryl ZnPc 6 by Triple Suzuki−Miyaura Cross-Coupling Reaction on α-Triiodo ZnPc 5. (b) Final Oxidation To Obtain the Target ZnPc 1
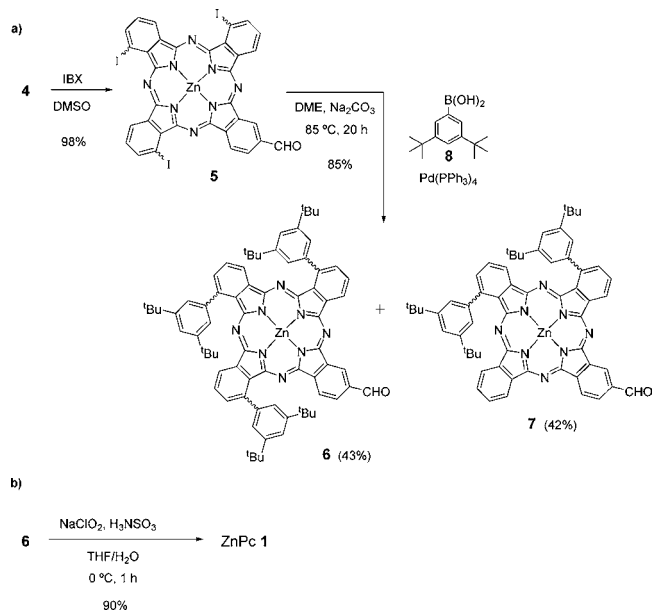
As for compound **4**, a mixture of eight regioisomeric Pcs is formed in almost equal amounts as clearly confirmed in the ¹H NMR spectrum of compound **5** (see Figure S6, Supporting Information) showing several singlets at 10.5 ppm assigned to the aldehyde, which all integrate for one proton.

Taking advantage of the good solubility of **5** in organic solvents, the Suzuki−Miyaura cross-coupling reaction was performed on this compound, employing 3,5-di-*tert*-butylphenylboronic acid (**8**)[12] and standard reaction conditions, giving rise to regioisomeric mixtures of α-triaryl- and α-diaryl-substituted ZnPcs **6** and **7** in 85% yield (Scheme 2a).

The steric restriction imposed by the introduction of two bulky aryl substituents pointing toward the same direction shows that, in a selective way, only four of the eight regioisomers of ZnPc **5** react to form the α-triaryl-substituted ZnPc **6**. Specifically, regioisomers **6a−d**, in which a single aryl group is pointing to the empty space of each Pc corner, are solely detected. Consequently, α-diaryl-substituted ZnPc **7**, which is in fact a mixture of seven regioisomers (see the Supporting Information), is formed from regioisomers **5e−h** bearing two iodine atoms pointing toward the same Pc corner, most probably by protonolysis of the intermediate palladium ZnPc complex formed by oxidative addition, that cannot evolve toward transmetalation with the bulky arylboronic acid.

By using sodium hypochlorite in the presence of sulfamic acid, ZnPc **6** was converted to ZnPc **1** as a mixture of regioisomers **a−d** in 90% yield (Scheme 2b). In column chromatography, three greenish blue bands were eluted quite separately (see the Supporting Information), whose structures were assigned to different regioisomers of the α-triaryl-β-carboxyZnPc **1**.

These regioisomers (**1a−d**) traveled through the column at different speeds, following the expected trend in the order of elution, that is, the more steric hindrance around the carboxylic acid group the less interaction with the stationary phase and, therefore, the faster elution from the column. Thus, the first

eluted band consisted of a mixture of regioisomers **1c** and **1d** having two aryl bulky groups pointing toward the carboxylic acid. The second one was assigned to **1b** and the last one to the **1a** presenting substantially reduced steric hindrance around the anchoring COOH group. ^{1}H NMR spectra of regiosomers **1a**, **1b**, and **1c/d** recorded in THF-d_8 showed remarkably well-resolved signals, indicating a low degree of aggregation of these carboxy ZnPcs at high concentration. Careful assignment of each spectrum was made by bidimensional NMR (COSY and 1D-ROESY) techniques (see the Supporting Information). In particular, the most characteristic signal in each spectrum was a singlet assigned to proton H$_1$ (Figure 2), which suffers a
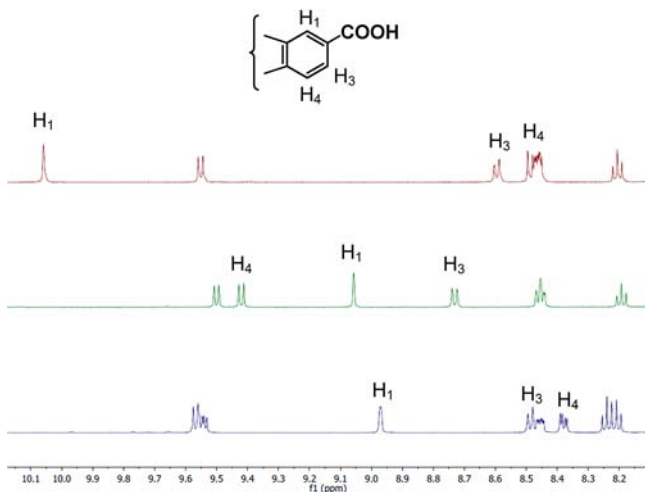

Figure 2. Partial ^{1}H NMR spectra (THF-d_8) of ZnPc **1a** (upper), **1b** (middle), **1c/d** (lower) (concn = 2.0×10^{-2} mol dm^{-3}).

significant chemical shift change depending on the structure. In the case of regioisomer **1a**, it appears at around 10 ppm, whereas it is high field shifted more than 1 ppm in the case of regioisomers **1b** and **1c/d** due to their close proximity to the diamagnetic current of a phenyl ring.

The absorption spectra of regiosomers **1a,b** and **c/d** recorded in THF showed features very similar to those of the **TT1** reference (Table 1). A strong Q-band absorption centered

Table 1. UV Spectra (THF) of ZnPc 1

	1a	1b	1c/d	TT1
Q-band (nm)	687	684	685	680

at 685 nm was observed (Figure 3), which is also a good indication of the appropriate electronic properties of these new phthalocyanines to be used as dyes in DSSCs. The fluorescence spectrum was recorded upon excitation at 685 nm (Q-band), observing the emission at 695 nm.

In summary, unsymmetrical A$_3$B-type α-triaryl-substituted zinc phthalocyanines have been prepared for the first time by an efficient convergent synthetic method, which implies a triple Suzuki−Miyaura cross-coupling reaction between an unsymmetrical α-triiodoZnPc derivative and an arylboronic acid. This method is high yielding and requires a low amount of expensive chemical reagents that are used only on the last steps of the synthesis. Moreover, selective formation of four of the eight possible α-triaryl-substituted ZnPc regioisomers is observed in the Pd-mediated cross-coupling reaction caused by the steric hindrance that would imply the introduction of two bulky aryl
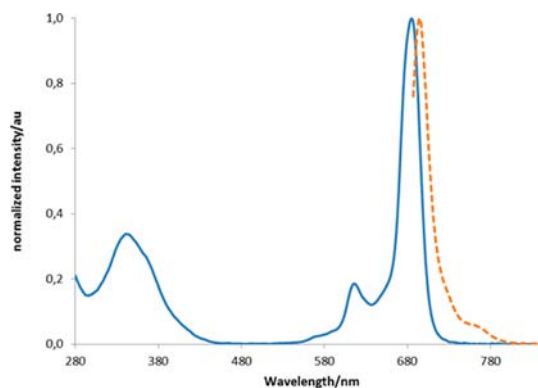

Figure 3. UV−vis absorption (solid line) and fluorescence (dashed line) spectra of ZnPc **1** (concn = 5.0×10^{-6} mol dm^{-3}) in THF.

groups pointing toward the same direction. The regioisomers were separated by simple column chromatography, thus allowing the isolation of regioisomerically pure β-carboxy-α-triarylZnPcs for the first time. These compounds are potential dyes to be incorporated in Grätzel solar cells since they fulfill the main requirement of suppressed macrocycle aggregation in solution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, product characterization, and COSY and 1D-ROESY spectra of ZnPc **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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