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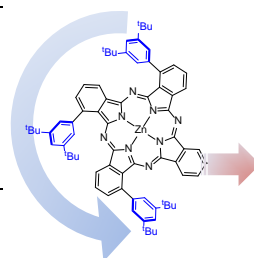
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# Convergent Strategy for the Regioselective Synthesis of Non-Aggregated $\alpha$ -Triaryl- $\beta$ -Carboxy Zinc Phthalocyanines

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**ABSTRACT:** A new design of non-aggregated 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  $\alpha$  positions of the macrocycle. The synthesis has been carried out following a convergent route in which the bulky aryl groups are introduced by Suzuki-Miyaura cross-coupling reaction on a preformed tri-iodophthalocyanine derivative. Two regioisomers of this  $\alpha$ -triaryl- $\beta$ -carboxyphthalocyanine could be isolated by column chromatography.



Phthalocyanines (Pcs)<sup>1</sup> 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.<sup>2</sup>

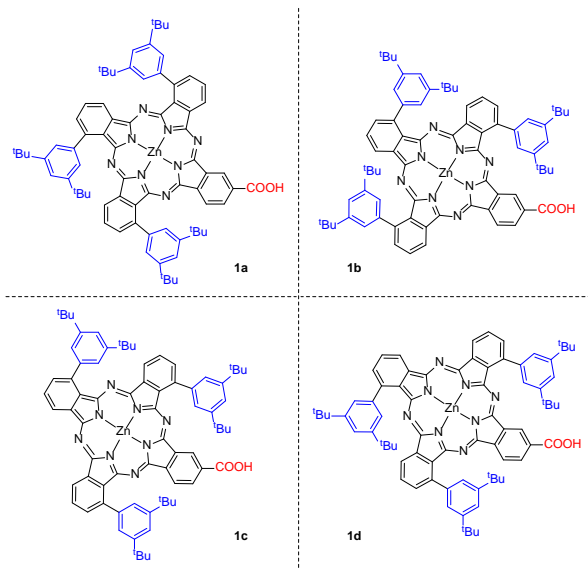
Previous work on zinc phthalocyanines has shown that the control over the formation of molecular aggregates onto the semiconductor nanoparticles, namely the TiO<sub>2</sub>, was key to achieve good efficiencies by preventing non-radiative deactivation of the dye in the excited state.<sup>3</sup> The 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  $\beta$ ) positions of the macrocycle, whereas the fourth isoindole unit was functionalized with an anchoring carboxylic group.<sup>4</sup> The particular success of the ZnPc named **TT1** and its derivatives<sup>5</sup> 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.

A further step was carried out from 2010<sup>6</sup> by incorporation of six very bulky 2,6-diphenylphenoxy groups at peripheral sites of a carboxyZnPc. Nowadays, ZnPcs with this substitution pattern, or related ones, have reached excellent efficiency values, close to 6.5%.<sup>7</sup> However, further research is still needed in order to optimize the performance of Pcs in this field.

Here, we describe a novel family of non-aggregated zinc(II) carboxyphthalocyanines with potential application in DSSCs, based on the introduction of bulky and rigid aryl substituents directly linked to the non-peripheral (or  $\alpha$ ) positions of the macrocycle, which will help to suppress aggregation. Moreover, a convergent synthetic strategy has been used, that in turn resulted in an effective selective method, with no precedent in Pc chemistry.

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

Ranta *et al.* have reported the regioselective preparation of the C<sub>4h</sub> isomer of tetrakis[3,5-di-*tert*-butylphenyl]-phthalocyanine by macrocyclization of the corresponding 3-aryl substituted phthalonitrile,<sup>8</sup> 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 towards the same Pc corner. In addition, single regioisomers of unsymmetrical A<sub>3</sub>B-type 1,8,15,22-substituted phthalocyanines have been selectively prepared by mixed macrocyclization of two different 3-arylsubstituted phthalonitriles bearing adequate sterically restricting aryl substituents. These results anticipated that our designed  $\alpha$ -triaryl- $\beta$ -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, it has never been reported the regioselective preparation of A<sub>3</sub>B-type Pcs with this substitution pattern.

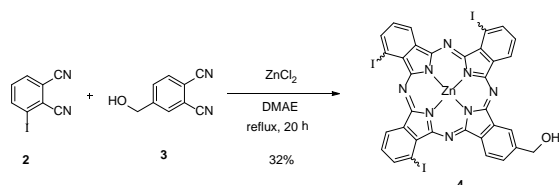


**Figure 1.** Possible regioisomers of the  $\alpha$ -triaryl- $\beta$ -carboxy ZnPc **1**.

Indeed, when a 4:1 molar mixture of the bulky  $\alpha$ -substituted 3-[3,5-di-*tert*-butylphenyl]phthalonitrile and the  $\beta$ -substituted 4-hydroxymethylphthalonitrile (**3**) was reacted using the conditions reported by Ranta *et al.* a mixture of regioisomeric ZnPcs was formed in low yield. Moreover, this method resulted quite tedious and expensive on account of the large amount of starting 3-[3,5-di-*tert*-butylphenyl]phthalonitrile that had to be prepared by a palladium-mediated coupling reaction.

Considering our previous experience on the functionalization of  $\beta$ -substituted iodoZnPcs by Pd-mediated reactions, we planned the preparation of target ZnPc **1** by a convergent synthetic strategy.<sup>9</sup> Thus, a 4:1 molar ratio mixture of 3-iodophthalonitrile (**2**)<sup>10</sup> and 4-hydroxymethylphthalonitrile (**3**)<sup>11</sup> was reacted at reflux in DMAE in the presence of ZnCl<sub>2</sub>. The desired A<sub>3</sub>B ZnPc **4** was obtained in 32% yield after isolation by column chromatography (Scheme 1). At this point, eight regioisomers of **4** were formed in equal amounts (see SI) whose separation by column chromatography was not feasible.

**Scheme 1. Cyclotetramerization reaction of phthalonitriles 2 and 3.**



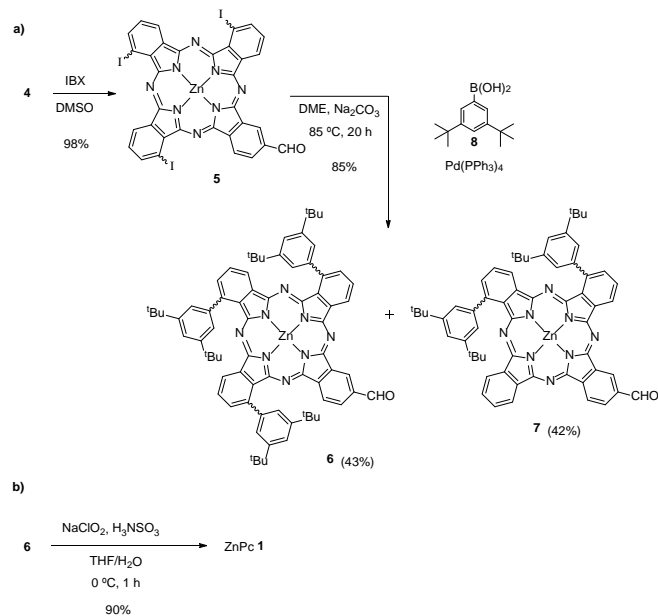
ZnPc **4** was then oxidized with the periodinane derivative IBX (1-hydroxy-1,2-benziodoxol-3(1H)-one 1-oxide) in DMSO to yield the formyl-derivative ZnPc **5** in 98% yield (Scheme 2). Taking advantage of the good solubility of **5** in organic solvents, the Suzuki-Miyaura cross-coupling reaction was performed on this compound, employing 3,5-di-*tert*-butylphenylboronic acid (**8**)<sup>12</sup> and standard reaction conditions, giving rise to regioisomeric mixtures of  $\alpha$ -triaryl- and  $\alpha$ -diarylsubstituted ZnPcs **6** and **7** in 85% yield. (Scheme 2a).

The steric restriction imposed by the introduction of two bulky aryl substituents pointing towards the same direction

causes that, in a selective way, only four of the eight regioisomers of ZnPc **5** react to form the  $\alpha$ -triarylsubstituted 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,  $\alpha$ -diarylsubstituted ZnPc **7** – which is in fact a mixture of seven regioisomers, see SI – is formed from “unreacted” regioisomers **5e-h** bearing two iodine atoms pointing towards the same Pc corner, most probably by protonolysis of the intermediate palladium ZnPc complex formed by oxidative addition, that cannot evolve towards transmetalation with the bulky arylboronic acid.

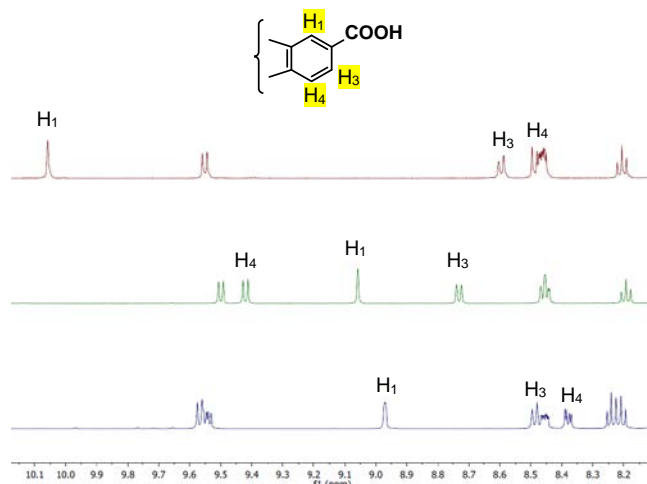
By using sodium hypochlorite in the presence of sulfamic acid, ZnPc **6** was converted to **1** as a mixture of regioisomers in 90% yield (Scheme 2b). In column chromatography, three greenish-blue bands were eluted quite separately (see SI), whose structures were assigned to different regioisomers of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

**Scheme 2. a) Convergent synthesis of  $\alpha$ -triaryl ZnPc 6 by triple Suzuki-Miyaura cross-coupling reaction on  $\alpha$ -triiodo ZnPc 5. b) Final oxidation to obtain the target ZnPc 1.**



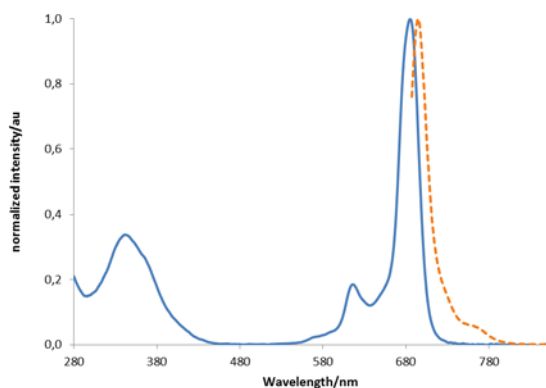
These regioisomers (**1a-d**) travelled through the column at different speeds, following the expected trend in the order of elution, that is, the more steric hindrance around the carboxylic acid group the less interaction with the stationary phase, and therefore, the faster elution from the column. Thus, the first eluted band consisted of a mixture of regioisomers **1c** and **1d** having two aryl bulky groups pointing towards 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. <sup>1</sup>H-NMR spectra of regioisomers **1a**, **1b** and **1c/d** recorded in d<sub>8</sub>-THF showed 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 SI). In particular, the most characteristic signal in each spectrum was a singlet assigned to proton H<sub>1</sub> (Figure 2), which suffers a 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**, **1c/d**, due to their close proximity to the diamagnetic current of a phenyl ring.



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

The absorption spectra of regioisomers **1a**, **b** and **c/d** recorded in THF showed very similar features to the **TT1** reference (Table 1). A strong Q band absorption centered around 685 nm was observed, which is also a good indication of the appropriate electronic properties of these new phthalocyanines to be used as dyes in DSSCs.



**Figure 3.** Absorption (solid line) and emission (dotted line) spectra of ZnPc **1** (concn =  $5.0 \times 10^{-6} \text{ mol dm}^{-3}$ ) in THF. Q band absorption centered at 685 nm and  $\lambda_{\text{em}}=695 \text{ nm}$ .

**Table 1.** UV spectra (THF) of ZnPc **1**.

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

In summary, unsymmetrical  $A_3B$ -type  $\alpha$ -triarylsubstituted 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  $\alpha$ -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  $\alpha$ -triarylsubstituted 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

groups pointing towards the same direction. The regioisomers were separated by simple column chromatography thus allowing the isolation of regioisomerically pure  $\beta$ -carboxy- $\alpha$ -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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### Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript

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## REFERENCES

- (1) (a) Martínez-Díaz, M. V.; Torres, T. In *Handbook of Porphyrin Science*; Kadish, K. M., Guillard, R., Smith, K. M., Eds.; World Science Publishers, **2010**, Vol. 10, Chapter 45, pp 141-181. (b) Martínez-Díaz, M. V.; de la Torre, G.; Torres, T. *Chem. Commun.* **2010**, 46, 7090.
- (2) (a) Mathew, S.; Yella, A.; Gao, P.; Humphry-Baker, R.; Curchod, B. F.-E.; Ashari-Astani, N.; Tavernelli, I.; Rothlisberger, U.; Nazeeruddin, M. K.; Grätzel, M. *Nat. Chem.* **2014**, 6, 242. (b) Yella, A.; Lee, H.-W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; Diau, E. W.-G.; Yeh, C.-Y.; Zakeeruddin, S. M.; Grätzel, M. *Science*, **2011**, 334, 629.
- (3) (a) Singh, V. K.; Kanaparthi, R. K.; Giribabu, L. *RSC Adv.* **2014**, 4, 6970. (b) Ragoussi, M.-E.; Ince, M.; Torres, T. *Eur. J. Org. Chem.* **2013**, 6475.
- (4) (a) Cid, J.-J.; Yum, J.-H.; Jang, S.-R.; Nazeeruddin, M. K.; Martínez-Ferrero, E.; Palomares, E.; Ko, J.; Grätzel, M.; Torres, T. *Angew. Chem. Int. Ed.* **2007**, 46, 8358. (b) Reddy, P. Y.; Giribabu, L.; Lyness, C.; Snaith, H. J.; Vijaykumar, C.; Chandrasekharam, M.; Lakshmikantham, M.; Yum, J.-H.; Kalayanasundaram, K.; Grätzel, M.; Nazeeruddin, M. K. *Angew. Chem. Int. Ed.* **2007**, 46, 373.
- (5) (a) Sharma, D.; Steen, G.; Korterik, J. P.; García-Iglesias, M.; Vázquez, P.; Torres, T.; Herek, J. L.; Huijser, A. J. *Phys. Chem. C* **2013**, 117, 25397. (b) García-Iglesias, M.; Cid, J.-J.; Yum, J.-H.; Forneli, A.; Vázquez, P.; Nazeeruddin, M. K.; Palomares, E.; Grätzel, M.; Torres, T. *Energy Environ. Sci.* **2011**, 4, 189. (c) García-Iglesias, M.; Yum, J. H.; Humphry-Baker, R.; Zakeeruddin, S. M.; Pechy, P.; Vázquez, P.; Palomares, E.;

Grätzel, M.; Nazeeruddin, M. K.; Torres, T. *Chem. Sci.* **2011**, *2*, 1145. (d) Cid, J. J.; García-Iglesias, M.; Yum, J. H.; Forneli, A.; Albero, J.; Martínez-Ferrero, E.; Vázquez, P.; Grätzel, M.; Nazeeruddin, M. K.; Palomares, E.; Torres, T. *Chem. Eur. J.* **2009**, *15*, 5130.

(6) (a) Matsuzaki, H.; Murakami, T. N.; Masaki, N.; Furube, A.; Kimura, M.; Mori, S. *J. Phys. Chem. C* **2014**, *118*, 17205. (b) Kimura, M.; Nomoto, H.; Suzuki, H.; Ikeuchi, T.; Matsuzaki, H.; Murakami, T. N.; Furube, A.; Masaki, N.; Griffith, M. J.; Mori, S. *Chem.-Eur. J.* **2013**, *19*, 7496. (c) Ragoussi, M.-E.; Cid, J.-J.; Yum, J.-H.; de la Torre, G.; Di Censo, D.; Grätzel, M.; Nazeeruddin, M. K.; Torres, T. *Angew. Chem. Int. Ed.* **2012**, *51*, 4375. (d) Kimura, M.; Nomoto, H.; Masaki, N.; Mori, S. *Angew. Chem. Int. Ed.* **2012**, *51*, 4371. (e) Mori, S.; Nagata, M.; Nakahata, Y.; Yasuta, K.; Goto, R.; Kimura, M.; Taya, M. *J. Am. Chem. Soc.* **2010**, *132*, 4054.

(7) (a) Ragoussi, M.-E.; Yum, J.-H.; Chandiran, A. K.; Ince, M.; de la Torre, G.; Grätzel, M.; Nazeeruddin, M. K.; Torres, T.

*ChemPhysChem* **2014**, *15*, 1033. (b) Ikeuchi, T.; Nomoto, H.; Masaki, N.; Griffith, M. J.; Mori, S.; Kimura, M. *Chem. Commun.* **2014**, *50*, 1941.

(8) Ranta, J.; Kumpulainen, T.; Lemmetyinen, H.; Efimov, A. *J. Org. Chem.* **2010**, *75*, 5178.

(9) Ince, M.; Cardinali, F.; Yum, J.-H.; Martínez-Díaz, M. V.; Nazeeruddin, M. K.; Grätzel, M.; Torres, T. *Chem. Eur. J.* **2012**, *18*, 6343.

(10) Leznoff, C. C.; Terekhov, D. S.; McArthur, C. R.; Vigh, S.; Li, J. *Can. J. Chem.* **1995**, *73*, 435.

(11) Enes, R. F.; Cid, J.-J.; Hausmann, A.; Trukhina, O.; Gouloumis, A.; Vázquez, P.; Cavaleiro, J. A. S.; Tomé, A. C.; Guldi, D. M.; Torres, T. *Chem. Eur. J.* **2012**, *18*, 1727.

(12) Heller, D. P.; Goldberg, D. R.; Wu, H.; Wulff, W. D. *Can. J. Chem.* **2006**, *84*, 1487.