

ABAB Phthalocyanines: Scaffolds for Building Unprecedented Donor– π –Acceptor Chromophores

Ettore Fazio,^[a] Javier Jaramillo-García,^[a] María Medel,^[a] Maxence Urbani,^[a, b, c] Michael Grätzel,^[c] Mohammad K. Nazeerudin,^{*,[d]} Gema de la Torre,^{*,[a]} and Tomas Torres^{*,[a, b]}

Dedicated to Michael Hanack on the occasion of his 85th birthday

Unique donor– π –acceptor phthalocyanines have been synthesized through the asymmetric functionalization of an ABAB phthalocyanine, crosswise functionalized with two iodine atoms through Pd-catalyzed cross-coupling reactions with ade-

quate electron-donor and electron-acceptor moieties. These push–pull molecules have been optically and electrochemically characterized, and their ability to perform as chromophores for dye-sensitized solar cells has been tested.

1. Introduction

Conjugated donor– π –acceptor ensembles are core structures for several purposes that range from basic research to real applications, namely, as mimics of the natural photosynthetic system,^[1] chromophores to study a wide variety of non-linear optical (NLO) phenomena,^[2] and active molecules in organic^[3] and hybrid dye-sensitized solar cells (DSSCs).^[4] In particular, the key to achieve highly efficient DSSCs lies in the preparation of stable organic dyes with an appropriate push–pull pattern that facilitates electron injection into the conduction band of a mesoporous TiO₂ semiconductor.^[5] In this regard, push–pull systems created with *meso*-substituted Zn^{II} porphyrins^[6] have shown a record power conversion efficiency of more than 13%

in DSSCs.^[7] These types of dyes present a linear arrangement between an electron-donor group and an electron-acceptor/anchoring moiety, with the porphyrin chromophore performing as an optically and electronically active conjugated unit. The key point for preparing such porphyrin compounds is the relatively easy accessibility to porphyrins with two *meso* positions functionalized with alkyl-substituted aryl groups, which afford solubility and avoid aggregation of the extended π -aromatic porphyrin surface, and two “free” *meso* positions. Selective electrophilic bromination at these free *meso* positions is crucial to widen the reactivity of these molecules, allowing their symmetric or asymmetric functionalization with many different donor and/or acceptor moieties by means of different metal-catalyzed coupling reactions.

The extraordinary optoelectronic characteristics of phthalocyanines (Pcs)^[8] have inspired researchers to design and synthesize specific push–pull Pc molecules as chromophores to study second-order NLO effects^[9] or as dyes for DSSCs.^[10] In particular, the most successful Pc dyes for DSSCs are Zn^{II}Pc derivatives functionalized with bulky, electron-donating groups at three isoindole units, and one electron-acceptor/anchoring unit at the other isoindole.^[11] These dyes also present a donor–acceptor pattern, but the donor and acceptor groups are not faced in a linear arrangement. Therefore, a challenge that remains unexplored is the preparation of face-to-face, push–pull Pcs. For that purpose, ABAC Pcs should be prepared or, more feasibly, appropriate face-to-face ABAB Pcs (see Figure 1), which could be further asymmetrically functionalized to give donor– π –acceptor derivatives. Conversely to porphyrin chemistry, the directed synthesis of face-to-face ABAB Pcs is still an issue as a consequence of the current lack of stepwise synthetic methodologies.^[12] On the other hand, statistical condensation of two different phthalonitrile precursors generally affords a mixture of the two possible isomers, namely, ABAB and AABB, which are frequently difficult to separate by chromatographic means.

[a] E. Fazio, J. Jaramillo-García, Dr. M. Medel, Dr. M. Urbani, Dr. G. de la Torre, Prof. T. Torres

Departamento de Química Orgánica
Universidad Autónoma de Madrid, 28049 Madrid (Spain)
E-mail: gema.delatorre@uam.es
tomas.torres@uam.es

[b] Dr. M. Urbani, Prof. T. Torres

IMDEA Nanociencia
c/Faraday, 9, 28049 Cantoblanco, Madrid (Spain)

[c] Dr. M. Urbani, Prof. M. Grätzel

Laboratory for Photonics and Interfaces
Institute of Chemical Sciences and Engineering
School of Basic Sciences, Swiss Federal Institute of Technology (EPFL)
1015 Lausanne (Switzerland)

[d] Prof. M. K. Nazeerudin

Group for Molecular Engineering of Functional Materials
Institute of Chemical Sciences and Engineering
School of Basic Sciences, Swiss Federal Institute of Technology (EPFL)
1951 Sion (Switzerland)
E-mail: mdkhaja.nazeeruddin@epfl.ch

Supporting Information and the ORCID identification number(s) for the author(s) of this article can be found under <http://dx.doi.org/10.1002/open.201600113>.

© 2016 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

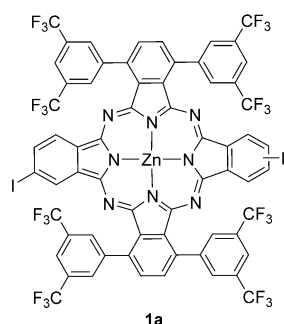


Figure 1. Structure of ABAB Porphyrin **1a**.

We have recently described the preparation of ABAB Pcs through the statistical condensation of bulky 3,6-bis-(3,5-bis(trifluoromethyl)phenyl)phthalonitrile, which is reluctant to give self-condensation, owing to the presence of rigid/bulky groups at the *o*-positions of the CN moieties, and iodo-containing phthalonitriles.^[13] In particular, ABAB Porphyrin **1a** (Figure 1) was successfully prepared in 16% yield. Importantly, the presence of two iodine atoms in crosswise isoindoles offers a unique opportunity to synthesize face-to-face, push-pull ABAC Pcs by metal-catalyzed coupling reactions, as well as to incorporate the Pc as a central block in multicomponent ensembles.

As a continuation of our previous work,^[13] we have explored the scope of the crosswise condensation by using several phthalonitriles, *o*-functionalized with different rigid/bulky substituents, which could also direct the crossed condensation with 4-iodophthalonitrile towards the formation of the corresponding ABAB Pcs. Also, this work is devoted to establishing these iodo-containing ABAB Pcs as unrivalled building blocks for the preparation of unprecedented face-to-face, push-pull

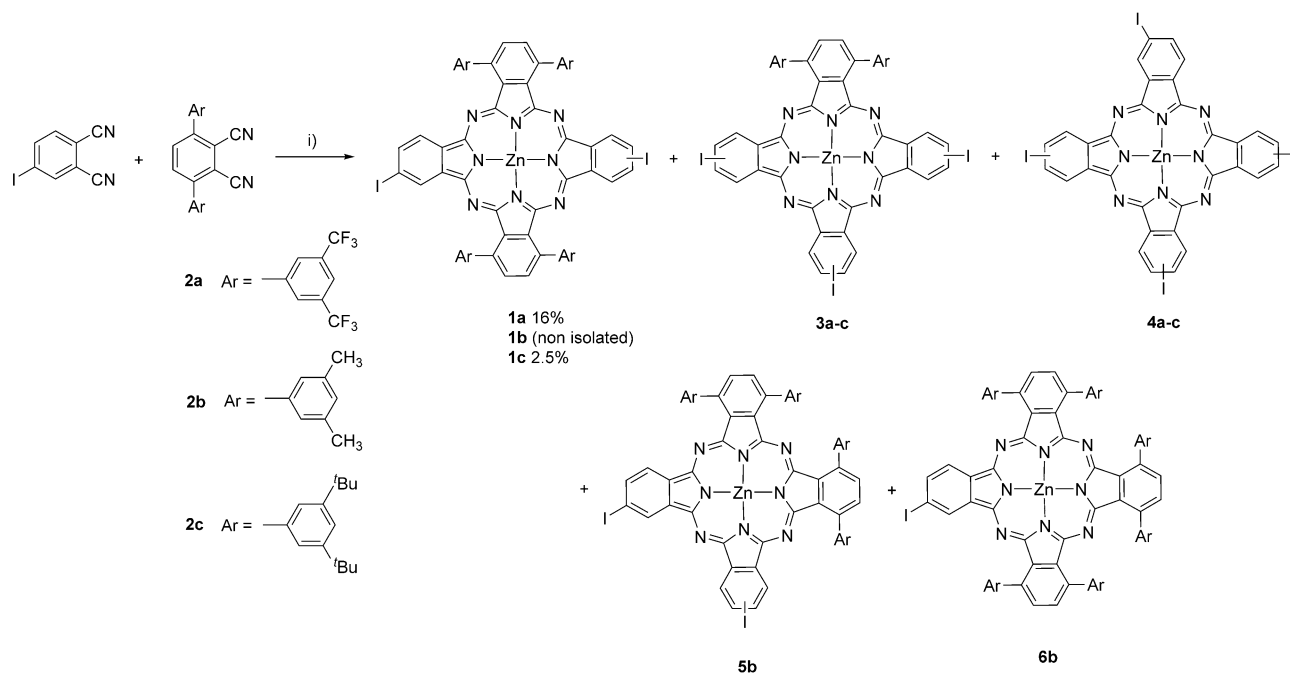
ABAC Pcs, which can be outstanding donor- π -acceptor chromophores for different purposes. In particular, we have prepared a series of Pcs functionalized with both electron-donating phenylamino groups and anchoring/electron-withdrawing carboxy groups in a face-to-face manner to determine the ability of these novel systems to perform as efficient sensitizers in DSSCs.

2. Results and Discussion

2.1. Synthesis of ABAB Phthalocyanines

3,6-Bis-(3,5-bis(trifluoromethyl)phenyl)phthalonitrile **2a** has proved very effective as a precursor for the preparation of ABAB Pcs (Scheme 1).^[13] Considering that octakis[α -aryl]Pcs have been prepared under certain conditions,^[14] it seems that functionalization with bare phenyl rings at the α -positions of the phthalonitrile precursor is not enough to avoid the formation of Pcs with adjacent phenyl-substituted isoindoles. Functionalization of the α -phenyl substituents with bulky, alkyl, or trifluoroalkyl moieties seems, in principle, necessary to more efficiently direct the reaction towards the formation of ABAB Pcs in crossed-condensation reactions.

Therefore, the preparation of phthalonitriles **2b** and **2c** functionalized with 3,5-dimethyl- and 3,5-di-*tert*-butylphenyl moieties, respectively, was accomplished by using a Pd^{II}-catalyzed Suzuki-Miyaura reaction between 3,6-bis-(tosylate)phthalonitrile^[15] and the corresponding boronic acids (Scheme S1). The crossed condensation of phthalonitriles **2b** and **2c** with 4-iodophthalonitrile (Scheme 1) was attempted under the reaction conditions optimized for the synthesis of **1a**^[13] (Table 1, entries 2 and 6). However, no traces of the desired products **1b** and **1c** were observed. In fact, using these conditions, only



Scheme 1. Statistical synthesis of Pcs **1a-c**.

Entry	Phthalonitrile	Conditions	Yield [%]
1	2a	Zn(OAc) ₂ , <i>o</i> -DCB/DMF (2:1)	16
2	2b	Zn(OAc) ₂ , <i>o</i> -DCB/DMF (2:1)	–
3	2b	Zn(OAc) ₂ , 1-pentanol, DBU	–
4	2b	Zn(OAc) ₂ , DMAE, DBU	8 ^[a]
5	2b	1) Li/1-pentanol 2) Zn(OAc) ₂	19 ^[a]
6	2c	Zn(OAc) ₂ , <i>o</i> -DCB/DMF (2:1)	–
7	2c	Zn(OAc) ₂ , DMAE, DBU	2
8	2c	1) Li/1-pentanol 2) Zn(OAc) ₂	–

[a] Mixture of ABAB and AABB isomers (**1b** and **5b**, Scheme 1).

the AB₃ Pcs **3b** and **3c** and B₄ Pcs **4b** and **4c** were obtained, with most of the corresponding bulky phthalonitriles **2a** and **2b** remaining unreacted in each case. In view of these results, other conditions were tested for the preparation of ABAB Pcs **1b** and **1c**. We observed that the two bulky phthalonitriles **2b** and **2c** performed rather differently. First, dimethylphenyl-functionalized phthalonitrile **2b** afforded condensation products in *N,N*-dimethylaminoethanol (DMAE) solvent (Table 1, entry 4), and also in the presence of lithium and pentanol; the latter conditions yielding a mixture of metal-free Pc derivatives that were further treated with Zn(OAc)₂ to obtain the corresponding Zn^{II}Pcs (Table 1, entry 5). In both cases, chromatographic separation of the mixture of Pcs and MS (MALDI-TOF) characterization of the different fractions confirmed that the second isolated fraction corresponded to the A₂B₂ derivative.

However, the lack of symmetry and the large splitting of the signals observed in the ¹H NMR spectrum of this fraction (as compared with the spectrum of **1a**), together with the fact that the first fraction eluted was identified by MS as the A₃B Pc **6b**, having three adjacent dimethylphenyl-substituted isoindoles, led us to conclude that the isolated A₂B₂ derivative was, indeed, a mixture of the two isomers **1b** and **5b** (Scheme 1). It is worth mentioning that the chromatographic separation of these two isomers was not possible.

On the other hand, di-*tert*-butylphenyl-functionalized phthalonitrile **2a** was much less reactive than its homologue **2b**. In fact, this phthalonitrile only contributed to form cross-conden-

sation products in DMAE (Table 1, entry 7), yielding a mixture of **1c**, **3c**, and **4c**, from which **1c** was isolated in a poor 2% yield.

The reactivity of phthalonitriles **2a–c** in competing self- and cross-condensation steps follows a logical trend in line with the van der Waals radius of the different bulky groups. In fact, the methyl groups do not possess the steric volume necessary to afford selectivity towards the formation of the opposite ABAB isomer **1b** versus the adjacent one, **5b**. On the other hand, the more bulky *tert*-butyl group helps to direct the reaction towards the ABAB Pc **1c**; however, the reactivity of *tert*-butyl-substituted phthalonitrile **2c** is also low for the crossed condensation with 4-iodophthalonitrile, thus resulting in a very poor yield of **1c**. Lastly, CF₃ is a rather bulky substituent with a van der Waals radius between that of the *i*Pr and *t*Bu groups,^[14] thus favoring crossed condensation between **2a** and 4-iodophthalonitrile for the formation of the crosswise Pc **1a**. Furthermore, the electron-withdrawing effect of CF₃ makes cyano moieties rather reactive, thus leading to good yields in the corresponding ABAB product **1a**.

In view of these results, Pc **1a** was selected as a platform for the construction of a series of push–pull Pcs, aiming at testing this approach as a feasible option to prepare efficient Pc dyes for DSSCs. Therefore, the preparation of novel push–pull Pcs **7–9** (Figure 2) was carried out through the asymmetric functionalization of Pc **1a** with electron-donating and anchoring/electron-withdrawing groups. Electron-donating groups that are present in efficient porphyrin photosensitizers were selected [i.e. *N,N*-dimethylaminophenylethynyl in **7** and bis(4-hexylphenyl)amino in **8** and **9**], together with ethynyl-bridged, electron-acceptor binding moieties that have previously been shown to facilitate the injection of photoexcited electrons from the Pc dyes to the TiO₂ in Pc-sensitized solar cells.^[11a,c,16]

First, the synthesis of **7** was accomplished through a former Sonogashira reaction with propargylic alcohol followed by a second Sonogashira coupling with 4-ethynyl-*N,N*-dimethylaniline (Scheme 2). Then, the one-step oxidation of the hydroxymethylethynyl derivate **11** under the reaction conditions described by Mazitsche et al.^[17] successfully afforded the target compound in an overall yield of 66%. It is worth mentioning that changing the reaction sequence, that is, coupling first the 4-ethynyl-*N,N*-dimethylaniline moiety, gave rise to lower overall yields.

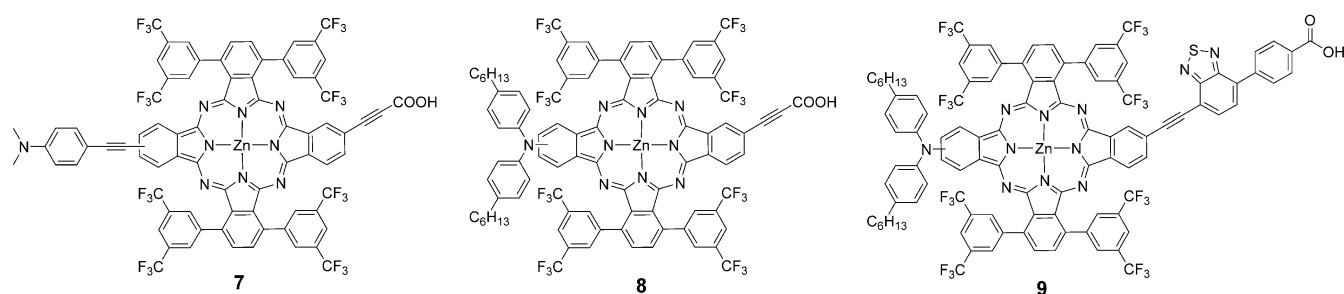
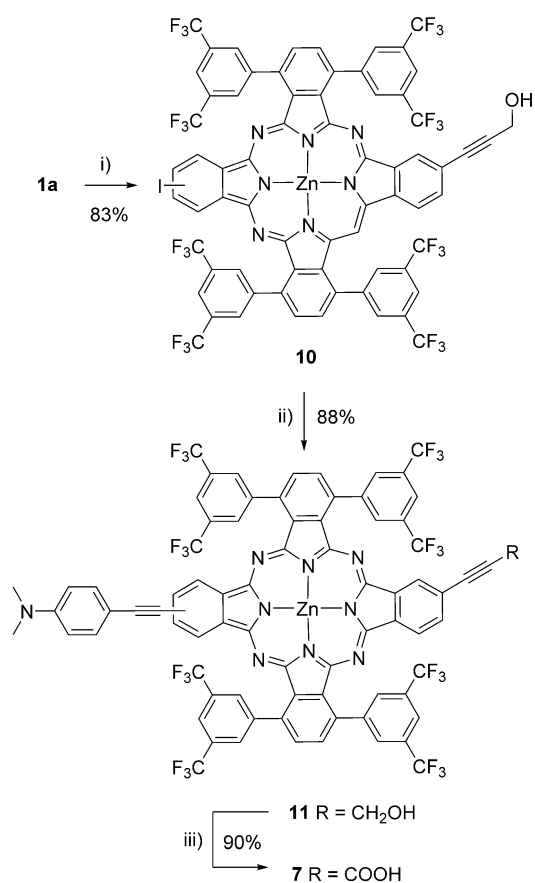
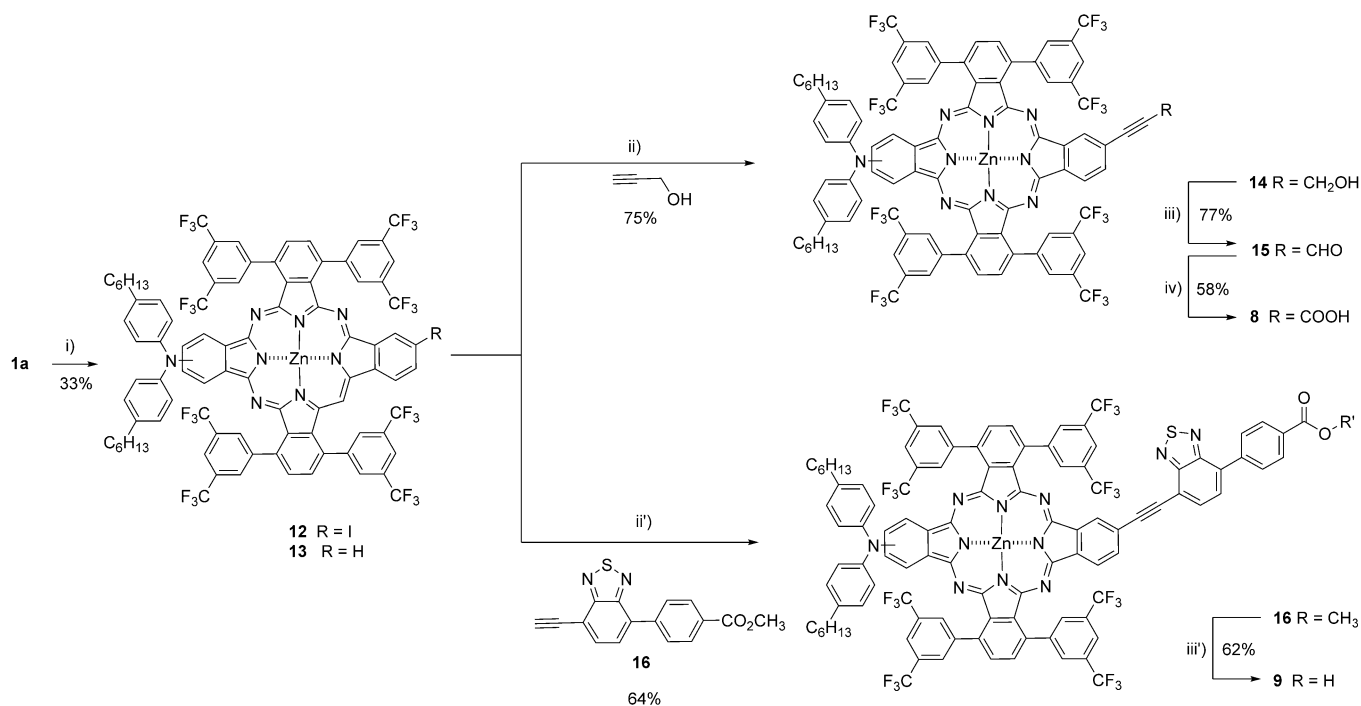


Figure 2. Structure of Pcs **7–9**.



Scheme 2. Synthesis of Pc 7. Conditions: i) propargylic alcohol, Pd(PPh₃)₄, CuI, NEt₃, THF; ii) 4-ethynyl-*N,N*-dimethylaniline, Pd(PPh₃)₄, CuI, NEt₃, THF; iii) IBX, THF, DMSO and then *N*-hydroxysuccinimide, THF, DMSO.

Similarly to the case of porphyrin sensitizers,^[8] Pcs 8 and 9 were functionalized with a stronger electron donor, that is, a directly linked diphenylamino unit. These compounds were more difficult to prepare. In both cases, it was necessary to first link the diphenylamino unit, as amination reactions over ethynyl-containing compounds (for instance, over 10) led to addition products over the triple bond in all cases. However, application of different Buchwald–Hartwig coupling conditions over 1a unceasingly afforded deiodinated compounds with no trace of the target *N*-coupled derivative 12 (Scheme 3). Finally, optimized conditions were found, namely, the use of Pd₂(dba)₃/tBu₃P and tBuONa in refluxing toluene, which yielded 12 contaminated with a related Pc derivative functionalized with two diphenylamino moieties and the deiodinated Pc derivative 13. A complete chromatographic separation of 12 from 13 could not be achieved, so it was necessary to set the following reactions (for the preparation of 8 and 9) with a mixture of the two products, as the deiodinated derivative would not react in the subsequently applied conditions. To prepare Pc 8, the same Sonogashira coupling conditions previously described for the synthesis of 11 were applied. The resulting hydroxymethylethynyl Pc derivative 14 was separated from the residues of deiodinated Pc 13, and was further oxidized in a two-step procedure (IBX/NaClO₂ with sulfamic acid) to obtain 8. Finally, the synthesis of the push–pull Pc dye 9 comprising a benzothiadiazole (BTD) bridge between the Pc core and the carboxyethynyl moiety (to increase the electron acceptor effect) was accomplished by a Sonogashira coupling between 12 and 17,^[18] followed by a basic hydrolysis of the ester group, which yielded the target compound (Scheme 3).



Scheme 3. Synthesis of Pcs 8 and 9. Conditions: i) Pd₂(dba)₃, tBu₃P, tBuONa, toluene; ii) Pd(PPh₃)₄, CuI, NEt₃, THF; iii) IBX, DMSO; iv) sulfamic acid, NaClO₂, THF; ii') Pd(PPh₃)₄, CuI, NEt₃, THF; iii') NaOH 20%, MeOH/THF.

2.2. Optical and Electrochemical Characterization

UV/Vis spectra of compounds **7–9** demonstrate a lack of aggregation of these Pcs in solution, owing to the presence of the rigid and bulky bis(trifluoromethyl)phenyl substituents (Figure 3). Notably, a bathochromic shift of the maximum

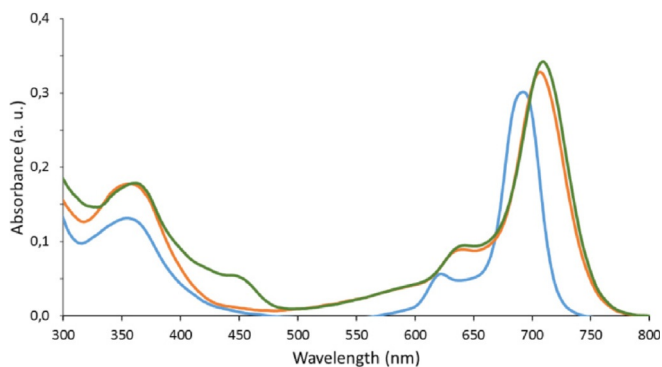


Figure 3. UV/Vis spectra of Pcs **7** (blue line, 8 μM), **8** (orange line 10 μM), and **9** (green line 7 μM) in THF.

wavelength (λ_{max}) of the Q band is observed from **7** (691 nm) to **8** (704 nm) and **9** (708 nm), owing to the stronger electron-releasing effect of the directly linked diphenylamino donor group, which destabilizes the HOMO level of the macrocycle (see the electrochemical results). The Q band of Pcs **8** and **9** is notably wider, yielding improved light-harvesting capabilities in the red region. The larger extinction coefficient of the Q band of Pc **9** is also remarkable, and similar to that previously observed in porphyrins containing the BTD unit.^[12] In the 500–600 nm region of the spectra for Pcs **8** and **9**, a weak and constant absorption is observed, which is absent in the spectrum of **7** and is probably a result of an electron-donating effect from the diphenylamino group to the Pc core. Noteworthy, a band at 448 nm is present also in the spectrum of **9**, and can be attributed to the BTD unit.^[7] Steady-state fluorescence spectra of compounds **7–9** were also recorded by exciting at the heights of the corresponding Q bands (Figure S1). Notably, the emissions of compounds **8** and **9** are notably quenched as a consequence of the strong electron donation from the directly linked dimethylamino group.

Electrochemical characterization of **7–9** was performed by using cyclic voltammetry in 0.1 M tetrabutylammonium phosphate (TBAP) CH_2Cl_2 solutions (Figure S2), using ferrocene as an external reference. The respective oxidation/reduction potentials, together with the HOMO/LUMO values, are summarized in Table 2. The first oxidation reactions of compounds **7–9** were reversible or quasi-reversible processes, with values in the range 0.42–0.26 V versus Fc/Fc^+ . The potential of compounds **8** and **9** are 120 and 160 mV lower than that of **7**, respectively, thus evidencing the strong impact that the direct linkage of the diphenylamino group has on the HOMO of the Pc macrocycle. On the other hand, the first reduction is irreversible for all of the compounds and occurs at very similar potentials, between -1.40 V (for **7**) and -1.45 V (for **9**) versus $\text{Fc}/$

Table 2. First oxidation and reduction potentials and HOMO/LUMO levels for Pcs **7–9**.

Pc	E [V vs. Fc/Fc^+]	E [V vs. Fc/Fc^+]	HOMO [eV vs. NHE]	LUMO [eV vs. NHE]
7	0.42 ^[a]	-1.40 ^[b]	1.06	-0.76
8	0.30 ^[c]	-1.37 ^[b]	0.94	-0.73
9	0.26 ^[c]	-1.35 ^[b]	0.90	-0.71

[a] Reversible. [b] Irreversible. [c] Quasi-reversible.

Fc^+ . Incorporation of the BTD unit between the Pc core and the COOH group in **9** has limited influence on the electronic properties of the Pc, namely, a slight stabilization of the HOMO and LUMO levels with regard to Pc **8** (Figure S3). Notably, the electrochemical HOMO–LUMO bandgap is consistent with the optical (E^{0-0}) bandgap obtained from the interception between the absorption and emission spectra (Figure S1).

2.3. Theoretical Calculations

DFT and TDDFT calculations have been performed to get insights into the electronic structure of the synthesized dyes (see the Supporting Information for details). First, the calculated absorption spectra of Pcs **7–9** (Figure S4) contains two distinct transitions in the zone of the Q band with significant donor-to-acceptor character. The first transition is characterized by a dominant HOMO→LUMO contribution, whereas the second has the HOMO→LUMO⁺¹ contribution as the most important. In all three dyes, the HOMO has extended delocalization toward the donor moiety (Figure 4). However, the LUMO has a slight delocalization onto the acceptor group for Pcs **7** and **8** and is rather centered in the Pc core for **9**, whereas the LUMO⁺¹ is completely centered in the Pc core for Pcs **7** and **9** and has a small delocalization toward the acceptor group in the case of **8** (Figure 4). The degree of delocalization of the LUMO and LUMO⁺¹ orbitals on the acceptor group is one of the factors considered to rationalize the photovoltaic behavior of these molecules, as mentioned below.

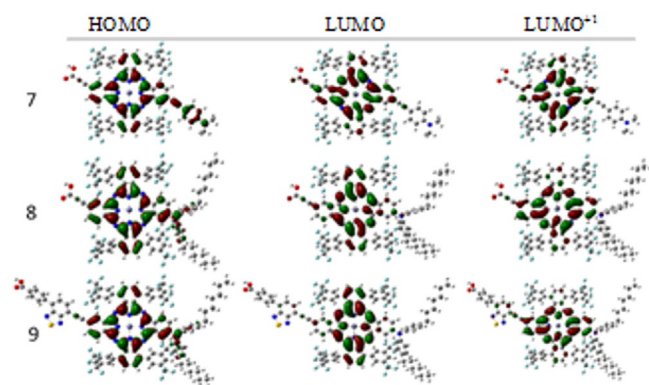


Figure 4. Contour plots for the HOMO (left), LUMO (center), and LUMO⁺¹ (right) of Pcs **7** (top), **8** (middle), and **9** (bottom) computed by using wB97xD/6-31G(d)/CPM(THF). Isovalue set to 0.02.

2.4. Photovoltaic Properties

Pcs 7–9 were tested in DSSCs on [9+4] μm thick TiO_2 films, which consist of a 9 μm thick active layer and an additional 4 μm thick scattering layer. For the preparation of the devices, the TiO_2 photoanodes were immersed in a 0.1 mM solution of the corresponding Pc in THF for 16 h. Table 3 summarizes the

Table 3. Dye-loading (<i>DL</i>) densities and photovoltaic data of the devices ^[a,b] made with Pc dyes on [9+4] μm thick TiO_2 films under simulated one sun illumination (AM1.5G) and active area of 0.159 cm^{-2} ^[c]					
Pc	<i>DL</i> [nmol cm^{-2}]	V_{OC} [mV]	J_{SC} [mA cm^{-2}]	<i>FF</i>	η [%]
7	87.1	386	8.16	0.61	1.92
7 + Cheno	–	339	0.991	0.63	0.21
8	26.1	427	9.88	0.58	2.43
9	14.1	411	4.46	0.60	1.09
(SM315) ^[d]	(83.5) ^[d]	(910) ^[d]	(18.1) ^[d]	(0.78) ^[d]	(13.0) ^[d]

[a] Four to five devices of equal quality were made for each dyes; the values obtained for the best cell are presented in each case. [b] Electrolyte is composed of 0.05 M iodide, 0.5 M lithium iodide and 0.5 M sodium iodine in acetonitrile. [c] The TiO_2 films have a total thickness of 13 μm consisting of a 9 μm thick TiO_2 active layer and an additional 4 μm of scattering layer. [d] Data derived from Ref. [7].

dye-loading densities and photovoltaic data obtained for the Pc-based DSSC devices. Pc 8 exhibits the best efficiency of the series (i.e. 2.43%), whereas the worst performing is Pc 9 ($\eta = 1.09\%$) (Table 3). As exemplified for Pc 7, the addition of co-adsorbent (CHENO) in the dye-uptake solution was attempted, but the performances of the devices were systematically much lower [especially a drop in the short-circuit current (J_{SC}) by a factor of ca. 10], which can be explained by a drastically reduced amount of adsorbed molecules on the photoanodes. It witnesses the remarkable low tendency of these Pcs to aggregate, thus making the use of co-adsorbents useless in the present cases.

To rationalize the different sensitization capability of these compounds, the responses of Pc 7 and Pc 8 are first compared. Both dyes have the same anchoring group and Pc core and differ only in the corresponding donor group. Pc 7, despite having both the most negative LUMO and positive HOMO (which, in principle, should confer to this sensitizer the best electron-injection and dye-regeneration efficiencies, respectively), displays a J_{SC} lower (8.16 mA cm^{-2}) than Pc 8 (9.88 mA cm^{-2}) and the poorest open-circuit voltage, V_{OC} (386 mV), of the series. On the other hand, the dye-loading density of Pc 8 was estimated to be three times lower than that of Pc 7, which can be explained by the strong steric repulsion induced by the bulky bis(hexyloxy)phenylamino group of Pc 8, which, hence, needs more space to accommodate on the TiO_2 surface than Pc 7 with a smaller 4-ethynyl-*N,N*-dimethylaniline moiety. Considering this fact, a superior J_{SC} should be expected for Pc 7. However, the opposite trend was observed, which is otherwise in agreement with the incident photon-to-current efficiency (*IPCE*) response observed for Pcs 7 and 8. In

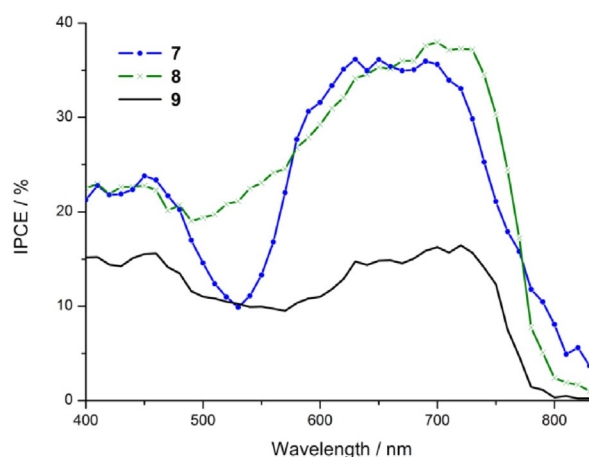


Figure 5. *IPCE* spectra of the DSSC devices made with Pcs 7–9.

accordance with their corresponding absorption spectra, the *IPCE* response of Pc 8 (Figure S9) is red shifted by about 50 nm with regard to that of Pc 7 (Figure 5). In addition, Pc 7 displays a significant drop in the *IPCE* response between 475 and 550 nm, whereas Pc 8 fulfills this valley much better. This factor may, in part, contribute to the difference observed in their J_{SC} values. Also, the degree of delocalization of the LUMO and LUMO⁺¹ orbitals onto the acceptor group is lower for Pc 7 (see Figure 4), which is consistent with its poorer injection. On the other hand, the lower V_{OC} obtained for Pc 7 can be ascribed to a faster electron recombination at the TiO_2 /electrolyte interface $e^-/(\text{TiO}_2\text{CB}) \leftrightarrow \text{I}_3^-$ (dark current), which should also contribute to lower the J_{SC} . The presence of the bulky amino group tethered with hexyl chains in Pc 8 (and as well in Pc 9) must better prevent the penetration of the oxidized species to the surface, thus reducing the dark current, a strategy commonly used and previously reported^[6b,11b] which is also coherent with the observed improved V_{OC} for Pc 8.

Next, the photovoltaic performances of Pc 8 and Pc 9, which differ only by the presence in the latter of an additional BTD bridge between the Pc and the acceptor group, are compared. Although the LUMO of Pc 9 is much less delocalized over the acceptor part (see Figure 4 and discussion above) and is slightly lower in energy than that of 8, these two factors might not be sufficient to solely explain the huge difference observed in the J_{SC} , which is almost half for Pc 9 (4.46 mA cm^{-2}) than that for Pc 8 ($J_{\text{SC}} = 9.88 \text{ mA cm}^{-2}$). An important contribution must arise from the difference in the amount of adsorbed dye molecule to the TiO_2 surface, which is twice as large for Pc 8 compared to Pc 9. Another possible contribution should come from faster recombination between oxidized dyes and photo-injected electrons in the TiO_2 conduction band caused by the BTD bridge in Pc 9, as previously reported.^[7,18] Although it was evidenced that the BTD unit tends also to increase the electron recapture by the charge carrier at the TiO_2 /electrolyte interface (i.e. dark current), the dark current seems to be similar for Pc 8 and Pc 9, as their V_{OC} values are also similar (427 and 411 mV, respectively), and thus it does not rationalize the different J_{SC} values. Most importantly, the *IPCE* values in the whole visible region are continually half for Pc 9 (ca. 10–15%) (Figure 5)

compared to that for **8** (ca. 20–35%) (Figure S11), matching well with the difference observed in the J_{SC} values.

3. Conclusions

We have proven that iodo-containing ABAB Pcs are versatile building blocks for the construction of unique donor- π -acceptor ensembles, in which the Pc core performs as an optically and electronically active π -spacer moiety. Although different bulky phthalonitriles have been tested as precursors to direct the reaction towards the formation of cross-condensation products in a reaction with 4-iodophthalonitrile, only 3,6-bis-(3,5-bis(trifluoromethyl)phenyl)phthalonitrile **2a** has been proven effective in providing the corresponding ABAB Pc (**1a**) in reasonable yields. For that reason, Pc **1a** was chosen as the starting material for the synthesis of unprecedented, cross-wise-functionalized, push-pull Pcs **7–9**. DSSCs prepared with these dyes show, in general, moderate conversion efficiencies, which can be ascribed to the fact that the LUMO of all of these Pcs is well-accommodated in the Pc core rather than in the electron-acceptor/anchoring group. This observation can be rationalized on the basis of the strong electron-acceptor character of the CF₃ moieties, which are otherwise necessary for the preparation of the starting iodo-containing ABAB Pc. Nevertheless, two conclusions can be attained from these studies. First, direct linkage of a diphenylamino (as donor group) and a carboxyethyl (as electron-acceptor/anchoring group) to the Pc core seems to be the most efficient functionalization; second, further improvements in the efficiency of Pc-sensitized DSSCs can, indeed, be achieved if electron-rich, crosswise-functionalized, push-pull Pcs are prepared. These results can be mostly considered as a proof of concept that establishes these novel donor-Pc-acceptor architectures as robust targets for the sensitization of TiO₂, as well as for other applications in which a donor- π -acceptor structure is required.

Experimental Section

Synthetic procedures, optical and electrochemical characterization, theoretical calculation details, and photovoltaic characterization are given in the Supporting Information.

Acknowledgements

The work was supported by the EU (GLOBASOL, FP7-ENERGY-2012J, 309194-2), the Spanish MINECO (CTQ-2014-52869-P) and Comunidad de Madrid (FOTOCARBON, S2013/MIT-2841).

Keywords: chromophores • dye-sensitized solar cells • phthalocyanines • push-pull • scaffolds

- [1] a) M. Gilbert, B. Albinsson, *Chem. Soc. Rev.* **2015**, *44*, 845–862; b) M. Natali, S. Campagna, F. Scandola, *Chem. Soc. Rev.* **2014**, *43*, 4005–4018; c) G. Bottari, G. de la Torre, D. M. Guldi, T. Torres, *Chem. Rev.* **2010**, *110*, 6768–6816.
- [2] M. Shimada, Y. Yamanoi, T. Matsushita, T. Kondo, E. Nishibori, A. Hatakeyama, K. Sugimoto, H. Nishihara, *J. Am. Chem. Soc.* **2015**, *137*, 1024–1027.
- [3] a) Y. Wu, W. Zhu, *Chem. Soc. Rev.* **2013**, *42*, 2039–2058; b) W. Ni, X. Wan, M. Li, Y. Wang, Y. Chen, *Chem. Commun.* **2015**, *51*, 4936–4950; c) B. Walker, C. Kim, T.-Q. Nguyen, *Chem. Mater.* **2011**, *23*, 470–482.
- [4] B.-G. Kim, K. Chung, J. Kim, *Chem. Eur. J.* **2013**, *19*, 5220–5230.
- [5] J. N. Clifford, E. Martinez-Ferrero, A. Viterisi, E. Palomares, *Chem. Soc. Rev.* **2011**, *40*, 1635–1646.
- [6] a) T. Higashino, H. Imahori, *Dalton Trans.* **2015**, *44*, 448–463; b) M. Urbani, M. Grätzel, M. K. Nazeeruddin, T. Torres, *Chem. Rev.* **2014**, *114*, 12330–12396.
- [7] S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin, M. Grätzel, *Nat. Chem.* **2014**, *6*, 242–247.
- [8] G. de la Torre, C. G. Claessens, T. Torres, *Chem. Commun.* **2007**, 2000–2015.
- [9] G. de la Torre, P. Vázquez, F. Agulló-López, T. Torres, *Chem. Rev.* **2004**, *104*, 3723–3750.
- [10] M. V. Martínez-Díaz, G. de la Torre, T. Torres, *Chem. Commun.* **2010**, *46*, 7090–7108.
- [11] a) M.-E. Ragoussi, J.-H. Yum, A. K. Chandiran, M. Ince, G. de la Torre, M. Grätzel, M. K. Nazeeruddin, T. Torres, *ChemPhysChem* **2014**, *15*, 1033–1036; b) M. Kimura, H. Nomoto, H. Suzuki, T. Ikeuchi, H. Matsuzaki, T. N. Murakami, A. Furube, N. Masaki, M. J. Griffith, S. Mori, *Chem. Eur. J.* **2013**, *19*, 7496–7502; c) M.-E. Ragoussi, J.-J. Cid, J.-H. Yum, G. de la Torre, D. Di Censo, M. Grätzel, M. K. Nazeeruddin, T. Torres, *Angew. Chem. Int. Ed.* **2012**, *51*, 4375–4378; *Angew. Chem.* **2012**, *124*, 4451–4454; d) M. Kimura, H. Nomoto, N. Masaki, S. Mori, *Angew. Chem. Int. Ed.* **2012**, *51*, 4371–4374; *Angew. Chem.* **2012**, *124*, 4447–4450; e) M. García-Iglesias, J.-J. Cid, J.-H. Yum, A. Forneli, P. Vázquez, M. K. Nazeeruddin, E. Palomares, M. Grätzel, T. Torres, *Energy Environ. Sci.* **2011**, *4*, 189–194.
- [12] G. de la Torre, C. G. Claessens, T. Torres, *Eur. J. Org. Chem.* **2000**, 2821–2830.
- [13] E. Fazio, J. Jaramillo-García, G. de la Torre, T. Torres, *Org. Lett.* **2014**, *16*, 4706–4709.
- [14] N. Kobayashi, T. Fukuda, K. Ueno, H. Ogino, *J. Am. Chem. Soc.* **2001**, *123*, 10740–10741.
- [15] M. J. Heeney, S. A. Al-Raqa, A. Auger, P. M. Burnham, A. N. Cammidge, I. Chambrier, M. J. Cook, *J. Porphyrins Phthalocyanines* **2013**, *17*, 649–664.
- [16] M. Ince, J.-H. Yum, Y. Kim, S. Mathew, M. Grätzel, T. Torres, M. K. Nazeeruddin, *J. Phys. Chem. C* **2014**, *118*, 17166–17170.
- [17] R. Mazitschek, M. Mülbauer, A. Giannis, *Angew. Chem. Int. Ed.* **2002**, *41*, 4059–4061; *Angew. Chem.* **2002**, *114*, 4216–4218.
- [18] A. Yella, C.-L. Mai, S. M. Zakeeruddin, S.-N. Chang, C.-H. Hsieh, C.-Y. Yeh, M. Grätzel, *Angew. Chem. Int. Ed.* **2014**, *53*, 2973–2977; *Angew. Chem.* **2014**, *126*, 3017–3021.

Received: September 22, 2016

Published online on December 27, 2016