Journal of Materials Chemistry C

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: J. Mater. Chem. C, 2021, 9, 10802

A versatile, divergent route for the synthesis of ABAC tetraazaporphyrins: molecularly engineered, push–pull phthalocyanine-type dyes†‡

Emre Güzel,[ab] Diana-Paola Medina,[a] María Medel,[a] Mehmet Kandaz,§[ac] Tomás Torres *[ade] and M. Salomé Rodríguez-Morgade *[ad]

A method to prepare key synthetic intermediates of ABAB- and ABAC-phthalocyanines and other tetraazaporphyrin analogues of interest for molecular electronics is described. These intermediates consist of ABAB-tetraazaporphyrins wherein the two B-subunits are endowed with iodine substituents at the *meta*-positions, whereas the substitution of the A-subunits is not conditioned to sterically demanding *ortho*-substituents, but rather can include a variety of functional groups at *meta*- or *ortho*-positions. The synthetic procedure includes the assembly of an ABAB tetraazaporphyrin by crossover cyclotetramerization of 5(6)-nitro-1,1,3-trichloroisoindolenine with a diiminoisoindoline or diimino-pyrroline derivative, followed by a three-step conversion of the two peripheral nitro groups into iodine substituents. The effectiveness of the method is based on two principles. On one hand, the inability of the trichloroisoindolenine derivative to self-condense, together with the mild reaction conditions, favors the preferential formation of an ABAB derivative, without conditioning the substitution at the pyrroline or isoindoline A-precursor. On the other hand, the opposite diiodo-tetraazaporphyrin can be easily functionalized through a variety of metal-catalyzed cross-coupling reactions, thus being a valuable synthetic intermediate for ABAB and ABAC tetraazaporphyrins. A molecularly engineered phthalocyanine-like dye, which features the prototypical structure of a donor–π-bridge–acceptor, was prepared using this method.

Received 2nd March 2021,
Accepted 17th May 2021

DOI: 10.1039/d1tc00990g

rsc.li/materials-c

Published on 17 maio 2021. Downloaded on 07/10/2024 07:18:29.

Introduction

Non-uniformly substituted tetraazaporphyrins comprise phthalocyanines or porphyrazines bearing different functional groups (represented by A, B, C and D in Fig. 1) at their isoindole or pyrrole moieties.[1] Despite the general definition, in practice, this category of porphyrinoids is almost exclusively constituted by tetraazaporphyrins that bear not more than two types of substituents at the pyrrolic subunits (AAAB, AABB and ABAB in Fig. 1). Compounds containing three (A, B and C) or four (A, B, C and D) different subunits are very desirable for manifold applications in fields of molecular electronics, but so far, satisfactory, general synthetic procedures for their preparation have been lacking.[2] The term ABAC also implies a specific arrangement of the substituents, referring to a structural

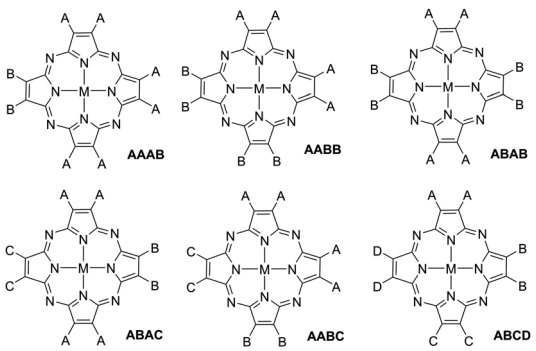


Fig. 1 General structures for non-uniformly substituted tetraazaporphyrins.

[a] Departamento de Química Orgánica Universidad Autónoma de Madrid Cantoblanco, 28049 Madrid, Spain. E-mail: salome.rodriguez@uam.es, tomas.torres@uam.es
[b] Department of Fundamental Sciences, Faculty of Technology Sakarya University of Applied Sciences, Sakarya, Turkey
[c] Department of Chemistry, Sakarya University, TR-54100 Adapazarı, Sakarya, Turkey
[d] Institute for Advanced Research in Chemical Sciences (IAdChem) Universidad Autónoma de Madrid Cantoblanco, 28049 Madrid, Spain
[e] Instituto Madrileño de Estudios Avanzados (IMDEA)-Nanociencia c/Faraday, 9 Cantoblanco, 28049 Madrid, Spain

† Dedicated to Professor Jaume Veciana and Professor Concepció Rovira on the occasion of their retirement.

‡ Electronic supplementary information (ESI) available. See DOI: 10.1039/d1tc00990g

§ M. Kandaz passed away in October 2017.

This journal is © The Royal Society of Chemistry 2021

Published on 17 maio 2021. Downloaded on 07/10/2024 07:18:29.

isomer bearing the same substitution (A) at two of the opposite pyrrole subunits, while the other two (B and C) contain different functionalizations and all the adjacent units are different to each other (see Fig. 1).

In the literature, there is a very limited number of methods to prepare non-uniformly substituted tetraazaporphyrins. The main obstacle lies in the scarce number of synthetic intermediates, which often constitute unstable species and offer a very limited variety of substitution patterns. Furthermore, their use does not necessarily provide acceptable yields of unsymmetric macrocycles either.[3] This is in stark contrast with porphyrins, for which useful dipyrrolic or tripyrrolic synthetic intermediates have been developed. However, for phthalocyanines or porphyrazines containing two types of substitution A and B, crossover cyclotetramerization of two differently functionalized phthalonitrile, maleonitrile, diiminoisoindoline or diiminopyrroline precursors constitutes the most widely used synthetic procedure. The latter affords a mixture of six compounds wherein four of them constitute non-uniformly substituted tetraazaporphyrins (the so-called AAAB, AABB, ABAB and ABBB tetraazaporphyrins) and the other two are symmetric macrocycles (AAAA and BBBB).[3]

The yield for each type of macrocycle depends upon statistical considerations,[2] the relative reactivity of the two precursors bearing A and B,[4,5] the used stoichiometry of reactants and the reaction conditions (*i.e.* metal template, solvent, temperature, *etc.*).[6] The target unsymmetric compound is obtained in moderate-to-very-low yields (0–40% in the best cases) after a laborious chromatographic separation that is not always possible. Crossover cyclotetramerization is particularly inefficient to prepare the opposite ABAB-isomers as they are statistically unfavoured (theoretically 12.5% against 25% of the adjacent AABB-isomer).[3,4,6] These elusive compounds can be prepared with reasonable yields by condensation of a trichloroisoindolenine derivative bearing B, with a diiminoisoindoline or diiminopyrroline derivative bearing A.[7,8] Although the method is not fully selective, the trichloroisoindolenine precursor cannot self-condense and, hence, the number of products decreases to three (ABAB, AAAB and AAAA). The limited scope of this method constitutes its major drawback, as trichloroisoindolenine derivatives are very labile,[9] and only unsubstituted[7] or nitro-substituted compounds[8,9b] have really shown some utility. The other procedure to prepare the opposite ABAB-tetraazaporphyrins involves the use of phthalonitrile or diiminoisoindolenine precursors with impediments to self-condense, because they are substituted at the *ortho*-positions with sterically demanding A moieties, such as *tert*-butyl,[6a] isopropoxy,[5] or benzene rings.[6b,10] However, the non-formation of sterically constrained macrocycles (that is, AAAA, AAAB and AABB) depends strongly on the reaction conditions and does not always guarantee acceptable yields of the ABAB compounds.[4a,6,10b]

It is easy to understand, based in the preceding considerations, that tetraazaporphyrins with triple (A, B and C) or quadruple (A, B, C and D) substitution patterns are almost non-existent, as more than two types of precursors generate very complex mixtures in crossover macrocyclizations (more than 15 compounds for triple and more than 35 compounds for quadruple patterns), which are impossible to separate. To the best of our knowledge, only an ABAC-type phthalocyanine has been prepared by a cyclotetramerization reaction. The compound was obtained in 9% yield by the reaction of two different diiminoisoindolines bearing the B and C substituents, respectively, and a trichloroisoindolenine bearing substituent A.[11] The other reported method to prepare ABAC-tetraazaporphyrins is based in the peripheral fabrication of a preformed ABAB macrocycle that contains reactive halogen substituents at the B subunits. This entails garnering important amounts of an ABAB precursor, a compound whose synthesis is problematic in itself. Nonetheless, there are some examples in the literature of preparations using palladium catalysed cross-coupling reactions at the halogen-functionalized opposite-isoindoles to afford the B and C subunits, while the A moieties contain bulky phenyl[10a] or 3,5-bistrifluoromethylphenyl substituents,[4b] respectively, at the *ortho*-positions. The latter proved to be essential for gathering sufficient ABAB precursor to work with. Again, the scope of these methods is very limited, since the design of other ABAC-systems is restricted to compounds containing 3,6-diphenyl- or 3,6-bis-(3,5-bistrifluoromethylphenyl)-substituted isoindoles as the A subunits.

In this work we have overcome this limitation. Thus, we wish to report a divergent procedure to prepare ABAC-tetraazaporphyrins, wherein the A substituents arise from a diiminoisoindoline or diiminopyrroline derivative, while the B and C substituents originate from the different derivatization of two iodo-substituted, opposite isoindoles, in an ABAB-precursor. As demonstrated by us and others, iodo-substituted phthalocyanines can be used in a variety of palladium catalysed reactions such as carboxylation,[12] alkynylation,[13–15] amination,[13,16] arylation,[13,17] vinylation,[15,18] or the introduction of phosphinic groups.[19] In the present work, the ABAB diiodo-tetraazaporphyrin precursor is prepared by reduction of two peripheral nitro groups, followed by a sequential diazotization reaction and iodide coupling in a preformed opposite isomer. The versatility and effectivity of our approach depends on three important conditions:

(i) The use of trichloroisoindolenine derivatives in the method to prepare the ABAB precursors; this ensures definite reliability to obtain enough amounts of the opposite isomer, precluding the formation of the statistically favoured adjacent isomer, which is also difficult to separate.[6b]

(ii) The use of 5(6)-nitro-1,1,3-trichloroisoindolenine as a starting material; this compound is more stable and is easier to handle than other trichloroisoindolenine derivatives, such as alkyl- and halogen-substituted compounds, as proved before.[9]

(iii) There is a wide range of functional groups that can be introduced as the A-type substitution, since the latter arises from a diiminoisoindoline or diiminopyrroline derivative; the synthesis of these precursors by reaction of the corresponding dinitrile with ammonia is well established[20] – indeed, just a quick search in Scifinder provides more than 440 of these derivatives, more than 150 of which are commercially available.

Therefore, we report here a convenient synthesis of ABAB-phthalocyanine analogues, endowed with two iodine atoms at

Published on 17 maio 2021. Downloaded on 07/10/2024 07:18:29.

the *meta*-positions of both opposite isoindole units. These compounds are intended to become general key precursors of highly asymmetric ABAC-phthalocyanines and other tetraazaporphyrins of interest in molecular electronics. As a proof of concept, we include the controlled synthesis of a push–pull, ABAC dibenzoporphyrazine, a molecularly engineered phthalocyanine-like dye, which features the prototypical structure of a donor–π-bridge–acceptor, in a linear arrangement. This type of disposition has been shown to be very effective in the design of dyes for dye-sensitized solar cells (DSSCs).[4b,21]

Results and discussion

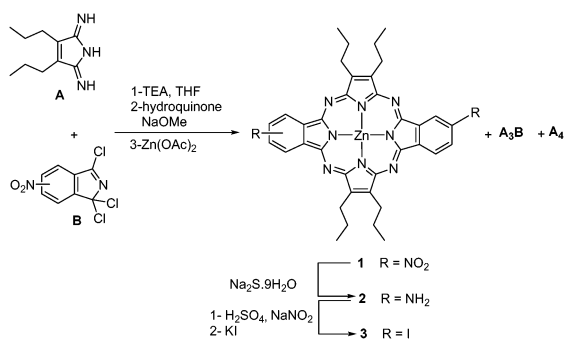
Synthesis of the diiodo-substituted ABAB intermediate

3,4-Dipropylpyrroline-2,5-diimine[22] was selected as the A moiety as it provides an A substitution pattern that is virtually inaccessible using the previously reported methods for ABAC systems. The opposite isomer of dinitrodibenzoporphyrazine (**1**, Scheme 1) was prepared following the reported procedure,[8a] consisting of the reaction of the diiminopyrroline with 5(6)-nitro-1,1,3-trichloroisoindolenine[23] at −40 °C in the presence of triethylamine.

This afforded a mixture of free base porphyrazines, with **1** and the A_3B benzoporphyrazine as the major compounds. The mixture was subsequently metallated with zinc(II) acetate (Scheme 1). The self-condensation of A to afford the symmetric A_4 porphyrazine was almost suppressed[24] most probably owing to the low temperature used for the reaction.[25]

The mixture of **1** and A_3B was treated with sodium sulfide, affording the diamine **2** and the corresponding A_3B monoamine, which were separated using column chromatography.[8a] Both **1** and **2** should consist of a *cis* and *trans* regioisomeric mixture of porphyrazines, owing to the unsymmetric nature of the 5(6)-nitro-1,1,3-trichloroisoindolenine. Indeed, the ^{13}C NMR spectrum of this precursor (Fig. 2) exhibits eight different double resonances, indicating the presence of both 5-nitro and 6-nitro-isomers. Judging by the similar intensity of the two components for the eight signals, a ∼1 : 1 ratio of the regioisomers can be inferred. Conversely, the presence of the two regioisomers for **2** could not be confirmed by NMR.

Porphyrazine **2** was subjected to a diazotization reaction by treatment with $NaNO_2$ in H_2SO_4, to afford the corresponding bis(diazonium) salt, which was *in situ* converted into the diiodo-porphyrazine **3** by treatment with KI. The efficiency of this process was very much influenced by the stoichiometry of the reactants and the reaction temperature (Table 1). Thus, the yield of isolated **3** could be optimized up to 36% by using 40 equivalents of KI at a temperature of −15 to −10 °C.



Scheme 1 Synthesis of the ABAB diiododibenzoporphyrazine precursor **3**.

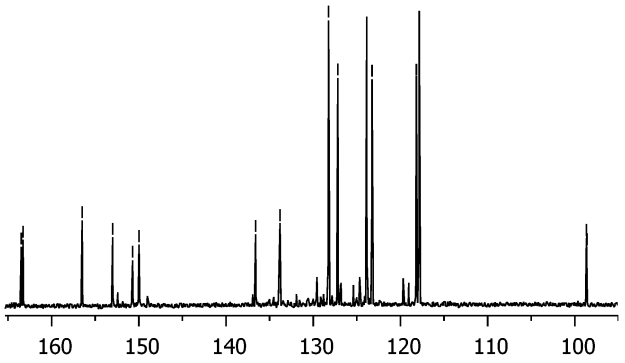


Fig. 2 ^{13}C NMR spectrum of 5(6)-nitro-1,1,3-trichloroisoindolenine indicating the presence of the regioisomeric mixture.

Table 1 Influence of the reaction conditions on the yield of **3** and (**3** : **4** : **5**) ratio

Equiv. of KI	T (°C)	Yield[a] of **3** (%)	**3** : **4** : **5**
4	−10 to +5	18	1 : 1 : 1
8	−10 to 0	22	2 : 1 : 1
20	−10 to −5	24	4 : 1 : 1
≥40	−15 to −10	36	10 : 1 : 0

[a] Yield of isolated compound.

A lower ratio of KI and/or higher temperatures led to different amounts of porphyrazines **4** and **5** (see Fig. 3), arising from the loss of one or both diazonium substituents under the reaction conditions. As indicated in Table 1, this side reaction could be minimized by carrying out the diazotization/substitution reaction under the above-mentioned conditions.

Compound **3** showed in ^1H NMR a doublet of doublets at 8.47 ppm (J = 8.0, 1.6 Hz) that is attributed to H^B (see Fig. S1, ESI‡). A second signal centred at 9.55 ppm is constituted by two overlying doublets (J = 1.6 Hz) assignable to H^A, while two other doublets (J = 8.0 Hz) centred at 8.97 and 8.98 ppm, respectively, are assigned to H^C. The splitting of the signals corresponding to H^A and H^C arises from the presence of the two *cis* and *trans* regioisomers for **3**, which seemed to be in a similar ratio. Likewise, all the aliphatic carbons and seven out of the ten non-equivalent aromatic carbons showed split signals in the ^{13}C NMR spectrum of **3** (Fig. S2, ESI‡). Separation of the two regioisomers using chromatographic techniques was not attempted for **3** and nor was it for any of the forthcoming regioisomeric mixtures. Using UV/Vis spectroscopy, the ABAB porphyrazine **3** showed a Q-band at λ_{max} = 626 nm with a full width at half maximum of 32 nm (see Fig. 5 below). For the ABAB and ABAC porphyrazines **5** and **4**, the corresponding Q-bands split into the corresponding Q_x and Q_y components,

 This journal is © The Royal Society of Chemistry 2021

Published on 17 maio 2021. Downloaded on 07/10/2024 07:18:29.

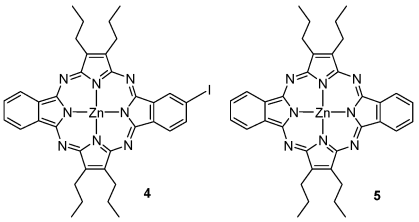


Fig. 3 Structures of tetraazaporphyrins **4** and **5**.

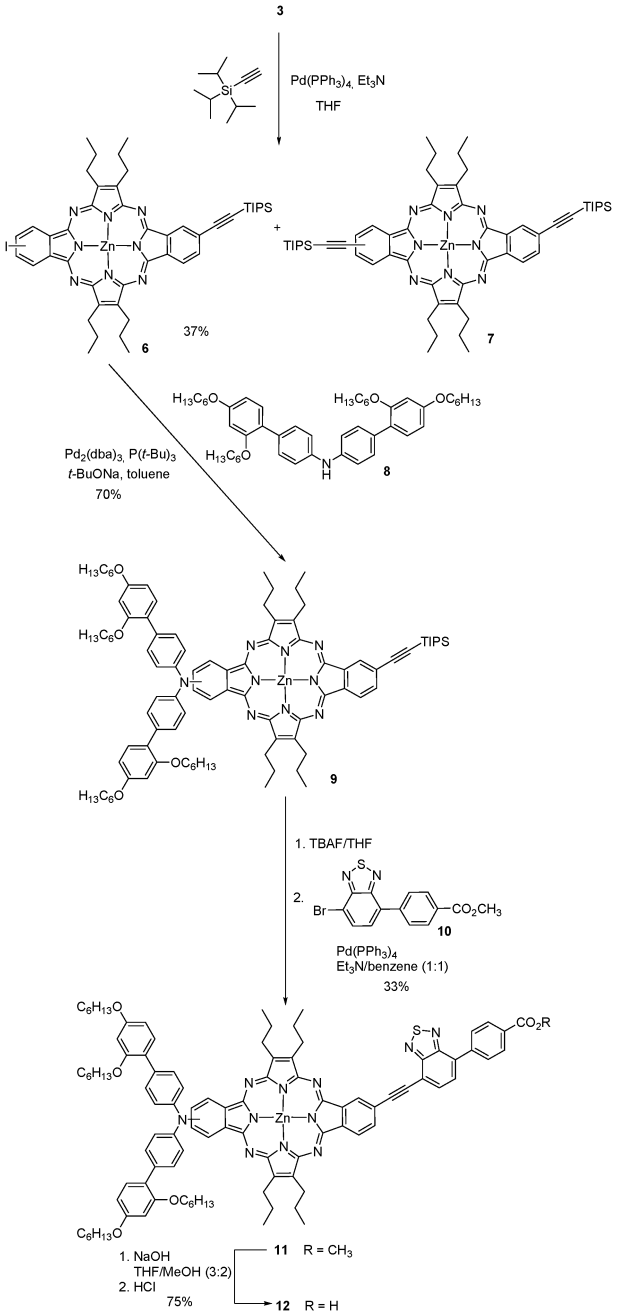
appearing at 651 and 615 nm for **5** and 643 and 618 nm for **4**, respectively (Fig. S13 and S9, ESI‡).

Synthesis of an ABAC donor–π-bridge–acceptor tetraazaporphyrin

Next, we used **3** as the precursor of an ABAC tetraazaporphyrin **12** (Scheme 2), the controlled synthesis of which would be inaccessible under the current state of the art. We selected functionalization at the periphery with these specific electron-donor and -acceptor substituents, as the corresponding porphyrin holding this linear donor–π-bridge–acceptor structure has shown outstanding photovoltaic performance in TiO_2-based DSSCs.[21]

The preparation of the related push–pull ABAC tetraazaporphyrin **12** is accessible by hydrolysis of the corresponding ester **11** (Scheme 2), which can be assembled using a three-step synthetic sequence from **3**. The three-step sequence consists of the introduction of an ethyne linker by Sonogashira coupling on one of the iodo functions of **3**, followed by functionalization with the electron-donor moiety **8** by Buchwald–Hartwig reaction on the opposite iodo substituent, and attachment of the electron-acceptor moiety **10** to the ethyne linker (Scheme 2).

The regioisomeric mixture of **3** was first subjected to a copper-free Sonogashira coupling with one equivalent of triisopropylacetylene, using $Pd(PPh_3)_4$ as the catalyst, in the presence of Et_3N, affording the monoethynyl-substituted macrocycle **6**, together with the disubstituted compound **7**. Porphyrazine **6** was isolated in 37% yield after column chromatography on silica gel. Fig. 4 displays the aromatic region of the ^{1}H NMR spectrum of **6**, which appears as six sets of resonances between 8.1 and 9.2 ppm, corresponding to the six different nuclei, designated as A, B, C, D, E, and F in the figure. The presence of the two regioisomers is clearly evidenced by the splitting of each set of signals. On one side, three broad singlets at 9.13, 9.11 and 9.05 ppm that integrate for two protons correspond to the two A, A′ and D, D′ types of protons (Fig. 4). Two doublets at 8.92 and 8.85 ppm (J = 8Hz) that integrate for one proton are assigned to C and C′, by analogy to the precursor **3**. The integration of this signal gives a 45 : 55 ratio for the *cis* and *trans* regioisomers, in line with our previous observations for the tetraazaporphyrin **3** and its trichloroisoindolenine precursor. B and B′ protons are observed at 8.26 ppm as a single doublet (J = 8Hz) integrating for one proton. The two doublets at 8.53 and 8.52 ppm (J = 7.5 Hz) are assigned to the F, F′ protons, while two doublets of doublets at 8.21 and 8.19 ppm (J = 1 Hz and J = 7.5 Hz) correspond to the



Scheme 2 Synthesis of the push–pull, ABAC-tetraazaporphyrin **12**.

E, E′ protons. The MS spectrum of **6** showed the cluster corresponding to the expected molecular ion at m/z = 951–957, accompanied by weaker ions at m/z = 1005–1011 and m/z = 790–795, assignable to **7** and deprotected **6**, respectively, which could be present as traces, since they were not detected by NMR. HRMS ($APCI^+$) confirmed the structure of **6** with a peak at m/z = 951.2724 corresponding to $[M + H]^+$ (Fig. S18, ESI‡).

Compound **7** displays a simpler ^{1}H NMR spectrum, with all the aromatic signals between 7.8 and 7.3 ppm, and a narrower multiplet (3.8–3.6 ppm) corresponding to the methylene protons directly attached to the pyrrole subunits. The molecular

Published on 17 maio 2021. Downloaded on 07/10/2024 07:18:29.

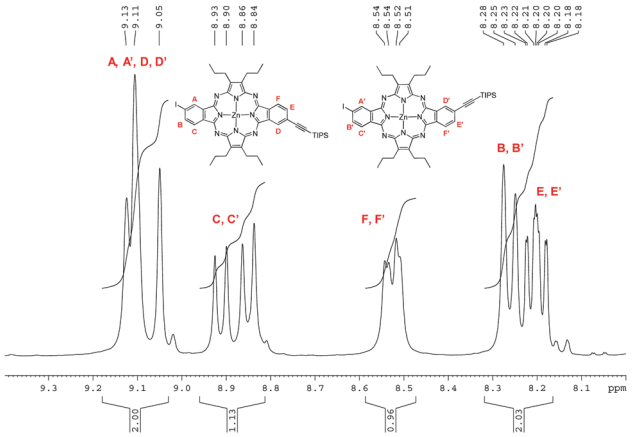


Fig. 4 ^{1}H NMR spectrum corresponding to the aromatic region of **6**.

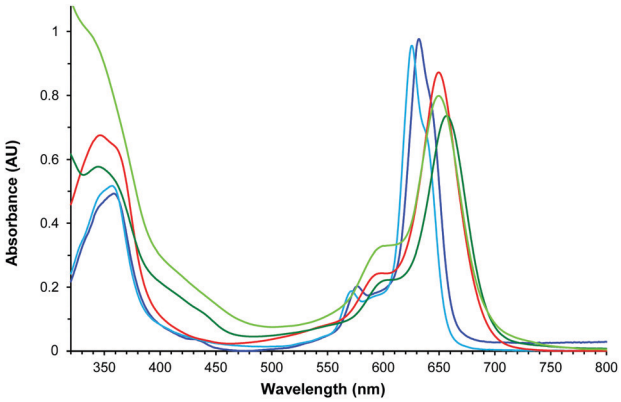


Fig. 5 Normalized UV/Vis spectra of **3** (navy blue), **6** (light blue), **9** (red), **11** (dark green) and **12** (light green) in $CHCl_3$.

ion $[M + H]^+$ appeared at m/z = 1005.5089 in HRMS ($APCI^+$) (Fig. S21, ESI‡).

The donor moiety consisted of the diarylamine **8**, which was prepared following reported procedures,[26] and attached to the tetraazaporphyrin **6** by Buchwald–Hartwig coupling, giving tetraazaporphyrin **9** in 70% yield. The structure of **9** was assessed by ^{1}H NMR and especially by HRMS (MALDI-TOF), which showed a peak at m/z = 1543.8604 corresponding to $[M]^+$ (Fig. S27, ESI‡).

The benzothiodiazole accepting unit **10**,[21,27] was incorporated to **9** by deprotection of the ethynyl linker with TBAF, followed by a Sonogashira coupling with the bromo derivative **10**. This afforded the push–pull tetraazaporphyrin **11** in 33% yield. Finally, saponification of **11**, followed by treatment with hydrochloric acid afforded **12** in 70% yield. Compounds **11** and **12** showed in MS (MALDI-TOF) the clusters corresponding to their molecular ions $[M]^+$ at m/z = 1656–1662 and 1642–1648, respectively. HRMS confirmed the structure of **12**, with a value of m/z = 1641.7414, which matches the theoretical value for this compound (1641.7412) (Fig. S34, ESI‡). Based on the ~1 : 1 regioisomeric mixture observed for the trichloroisoindolenine precursor and the tetraazaporphyrin intermediates **3** and **6**, we assume that both compounds **11** and **12** consist of *cis* and *trans* regioisomeric mixtures, although this could not be confirmed spectroscopically.

Fig. 5 displays the absorption spectra in $CHCl_3$ of tetraazaporphyrin **12**, and its synthetic intermediates **3**, **6**, **9** and **11**. Despite their non-symmetric ABAB or ABAC structures, all the compounds exhibit non-split, though broad, Q-bands.[28] As a general feature, compounds **9**, **11**, and **12**, containing the amine function (red and light- and dark-green lines, respectively, in Fig. 5), exhibit broader (full width at half maximum of 41–44 nm) and red-shifted Q-bands (λ_{max} = 650–657 nm *vs.* λ_{max} = 626–632 nm for macrocycles **3** and **6**). This reflects the extension of the conjugation through the amine group.

DFT calculations for the *trans* isomer of **12** were performed at the B3LYP/6-31G(d,p) level, using the GAUSSIAN 09 package.[29] The frontier orbitals estimated for **12** are represented in Fig. 6.

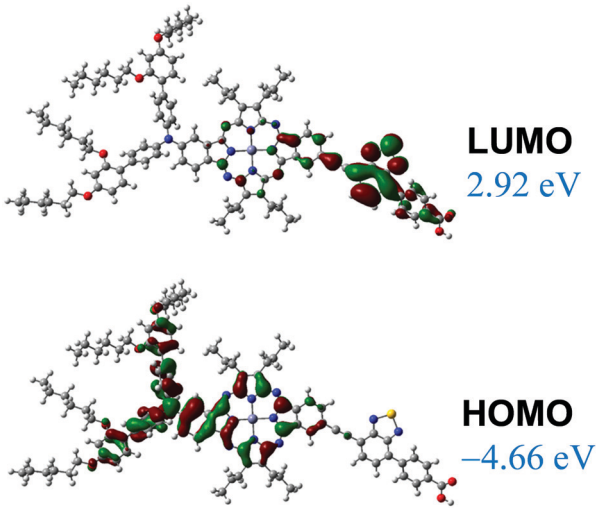


Fig. 6 HOMO and LUMO orbitals of the *trans* isomer of **12** calculated using DFT (B3LYP/6-31G (d,p)).

As for the parallel porphyrin,[21] compound **12** shows a high degree of orbital partitioning. Thus, the HOMO orbital is predominantly localized on the macrocycle and the donor moiety. By contrast, the LUMO orbital is fully localized on the accepting unit, showing a high density in the BTD ring. Hence, the HOMO–LUMO transition should have a considerable CT character for this regioisomer.

Experimental

Instrumentation and materials

Commercially available solvents and reagents were used without further purification unless otherwise mentioned. For anaerobic and/or anhydrous reactions, solvents were dried by distillation with Na/benzophenone (THF), or by treatment with previously activated molecular sieves (3 or 4 Å), or with an Innovative Technology Inc. MD-4-PS system. The air-sensitive reactions were carried out using standard Schlenk techniques. Column chromatography was carried out on silica gel Merck-60

 This journal is © The Royal Society of Chemistry 2021

Published on 17 maio 2021. Downloaded on 07/10/2024 07:18:29.

(230–400 mesh, 60 Å), and TLC on aluminum sheets precoated with silica gel 60 F254 (E. Merck). Size exclusion chromatography was performed using Bio-BeadsTM S-X1 apparatus. UV-vis spectra were recorded using a JASCO V-660 spectrometer. MS experiments were performed by the Servicio Interdepartamental de Investigación (SIdI) at the Autónoma University of Madrid. EI spectra were obtained using a Waters GCT Agilent Technologies 6890N spectrometer, FAB spectra were obtained with a Waters VG AutoSpec spectrometer and MALDI-TOF-MS spectra were obtained using a BRUKER ULTRAFLEX III instrument equipped with a nitrogen laser operating at 337 nm. NMR spectra were recorded using BRUKER AC-300 (300 MHz) or Bruker XRD-500 (500 MHz) instruments. The temperature was actively controlled at 298 K. Chemical shifts are measured in ppm relative to the corresponding deuterated solvent. Carbon chemical shifts are measured downfield from TMS using the resonance of the deuterated solvent as the internal standard. Infrared spectra (IR) were recorded using a Bruker Vector 22 instrument. Porphyrazines **1** and **2**,[8a] diarylamine **8**[26] and thiadiazole **10**[21,27] were prepared following the reported procedures.

Zn(II) [2,3-12,13-bis(benzo-4′(5′)-iodo)-7,8,17,18-tetrapropylporphyrazinato] (3)

A suspension of porphyrazine **2**[8a] (100 mg, 0.15 mmol) in 2.5 M H_2SO_4 (2 mL) and dry THF (1 mL) was cooled at −15 °C and a solution of $NaNO_2$ (180 mg, 2.59 mmol) in water was added dropwise under stirring. After total addition, the mixture was further stirred for 30 min at −10 °C and then poured over a solution of KI (2 g, 12.05 mmol) in cold water (1 mL). The resulting mixture was stirred for 45 min at the same temperature, and after that the blue solid was filtered, washed with water, and dissolved in THF (20 mL). The solution was subsequently washed with a saturated solution of $Na_2S_2O_3$ (10 mL), water (15 mL) and dried over Na_2SO_4. After filtration of the drying agent, the solvent was rotary evaporated and the blue solid purified by column chromatography on silica gel using a 50 : 1 mixture of toluene/pyridine. The first fraction was collected affording a blue solid that was washed with methanol to give 46 mg (36%) of **3**. ^{1}H NMR (300 MHz, THF-d_8): δ (ppm) = 9.55 (2d, J = 1.6 Hz, 2H), 8.98, 8.97 (2d, J = 8.0 Hz, 2H), 8.47 (dd, J = 8.0, 1.6 Hz, 2H), 3.9–3.8 (m, 8H), 2.4–2.3 (m, 7H), 1.3–1.2 (m, 12H). ^{13}C NMR (75.5 MHz, THF-d_8): δ (ppm) = 158.46, 158.38, 158.30, 158.21, 153.49, 153.40, 152.63, 152.51, 144.69, 144.64, 139.20, 138.69, 132.56, 124.95, 96.09, 29.09, 28.97, 26.57, 26.34, 15.31, 15.24. FTIR (KBr): ν (cm^{-1}) = 3063 (Ar-H), 2956, 2865 (R-H), 1597, 1454, 1365, 1291, 1261, 1134, 1103, 1002, 897, 822, 760, 750. UV-vis (THF): λ_{max} (nm) ($\log \varepsilon$ (dm^3 mol^{-1} cm^{-1})) = 639 (sh), 626 (3.90), 571 (3.19), 357 (3.63). MS (MALDI-TOF, DCTB): m/z = 896–901 $[M]^+$. HRMS: m/z = 896.0248; calculated for $[C_{36}H_{34}I_2N_8Zn]$: 896.0282.

Zn(II) [2,3(benzo-4′-iodo)-12,13-benzo-7,8,17,18-tetrapropylporphyrazinato] (4)

When the above-described diazotization and substitution reactions were performed using 4 equivalents of KI at a temperature range of −10 to +5 °C, three fractions were collected by column chromatography. The second fraction afforded **4** in 18% yield. ^{1}H NMR (300 MHz, THF-d_8): δ (ppm) = 9.63 (d, J = 3Hz, 1H), 9.34–9.31 (m, 2H), 9.06 (d, 6Hz, 1H), 8.45 (dd, J = 6Hz, 2Hz, 1H), 8.16–8.13 (m, 2H), 4.0–3.9 (m, 8H), 2.5–2.4 (m, 8H), 1.4–1.3 (m, 12H). FTIR (KBr): ν (cm^{-1}) = 3050 (Ar-H), 2954, 2927, 2867 (R-H), 1598, 1477, 1454, 1366, 1329, 1291, 1132, 1102, 1005, 952, 893, 819, 761, 746, 704. UV-vis (THF): λ_{max} (nm) ($\log \varepsilon$ (dm^3 mol^{-1} cm^{-1})) = 643 (3.61), 618 (3.76), 592 (sh), 566 (3.05), 352 (3.54). MS (MALDI-TOF, DCTB): m/z = 770–775 $[M]^+$.

Zn(II) [2,3-12,13-dibenzo-7,8,17,18-tetrapropylporphyrazinato] (5)

The third eluted fraction afforded **5** in ∼18% yield. This compound was contaminated with **4**. The spectroscopic data are taken from the mixture of the two compounds. ^{1}H NMR (300 MHz, THF-d_8): δ (ppm) = 9.31–9.28 (m, 4H), 8.13–8.11 (m, 4H), 3.94 (t, J = 9Hz, 8H), 2.4–2.3 (m, 8H), 1.3–1.1 (m, 12H). FTIR (KBr): ν (cm^{-1}) = 3081, 3054 (Ar-H), 2957, 2926, 2869 (R-H), 1716, 1645, 1597, 1527, 1477, 1455, 1337, 1289, 1102, 1004, 758, 744, 702. UV-vis (THF): λ_{max} (nm) ($\log \varepsilon$ (dm^3 mol^{-1} cm^{-1})) = 651 (3.52), 632 (sh), 615 (3.48), 595 (sh), 578 (sh), 559 (sh), 349 (3.53). MS (MALDI-TOF, DCTB): m/z = 644–649 $[M]^+$.

Zn(II) [2,3-(benzo-4′-ethynyltriisopropylsilane)-12,13-(benzo-4″(5″)-iodo)-7,8,17,18-tetrapropylporphyrazinato] (6)

A mixture of **3** (100 mg, 0.1 mmol), triisopropylacetylene (25 μL, 0.1 mmol), $Pd(PPh_3)_4$ (6.4 mg, 0.05 eq.), dry THF (10 mL) and dry Et_3N (2 mL) wa gently refluxed under Ar for 4 h. Afterwards, the solvent was rotary evaporated and the residue was chromatographed on Biobeads using toluene as the eluent. The first fraction contained compound **6** (34 mg, 37%), which was obtained as a blue-greenish solid. ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.13–9.05 (m, 2H), 8.92–8.84 (m, 1H), 8.54–8.51 (m, 1H), 8.26–8.24 (m, 1H), 8.21–8.19 (m, 1H), 3.23 (m, 8H), 2.02 (m 8H), 1.26–1.16 (m, 30H), 0.93–0.81 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) = 143.48, 143.42, 143.41, 143.20, 138.30, 137.74, 137.48, 137.17, 133.00, 131.49, 131.43, 131.36, 129.87, 129.74, 127.67, 127.51, 126.24, 124.37, 124.34, 123.67, 123.63, 122.36, 108.58, 95.49, 92.82, 32.09, 29.86, 29.52, 27.98, 27.91, 27.79, 25.41, 22.85, 19.15, 15.06, 15.02, 14.27, 11.85. FTIR (KBr): ν (cm^{-1}) = 3049, 3025 (Ar-H), 2956, 2928, 2866 (R-H), 1720, 1670, 1580, 1457, 1375, 1290, 1264, 1217, 1087, 1042, 803, 738, 697. UV-vis ($CHCl_3$): λ_{max} (nm) ($\log \varepsilon$ (dm^3 mol^{-1} cm^{-1})) = 644 (sh), 632 (3.87), 577 (3.18), 440 (sh), 358 (3.57). HRMS ($APCI^+$): m/z = 951.2724; calculated for $[C_{47}H_{56}IN_8SiZn]$: 951.2728 $[M + H]^+$.

Zn(II) [2,3-12,13-bis(benzo-4′(5′)-ethynyltriisopropylsilane)-7,8,17,18-tetrapropylporfirazinato] (7)

The disubstituted compound **7** (5 mg, 5%) was isolated from the second fraction of the column chromatography. ^{1}H-NMR (300 MHz, $CHCl_3$): δ (ppm) = 7.8–7.3 (m, 6H), 3.8–3.6 (m, 8H), 2.2–2.1 (m, 36H), 1.9–1.8 (m 8H), 1.3–1.2 (m, 12H), 0.9–0.8 (m, 6H). UV-vis ($CHCl_3$): λ_{max} (nm) ($\log \varepsilon$ (dm^3 mol^{-1} cm^{-1})) = 6.34 (3.98), 5.79 (3.32), 355 (3.68), 3.42 (sh). HRMS ($APCI^+$): m/z = 1005.5089; calculated for $[C_{58}H_{77}N_8Si_2Zn]$: 1005.5096 $[M + H]^+$.

Published on 17 maio 2021. Downloaded on 07/10/2024 07:18:29.

Zn(II) [2,3-(benzo-4′(5′)-ethynyltriisopropylsilane)-12,13-(benzo-4″-bis(2′,4‴-dihexoxybiphenyl-4-yl)amine)-7,8,17,18-tetrapropylporphyrazinato] (9)

To a deaerated Schlenk tube charged with **6** (20 mg, 0.02 mmol), diarylamine **8** (19.5 mg, 1.5 eq.), $Pd_2(dba)_3$ (0.17 mg, 0.01 eq.), tri-*t*-butylphosphine (0.11 mg, 0.03 eq.) and *t*-BuONa (4.3 mg, 2.5 eq.), deaerated, anhydrous toluene (2 mL) was added. The suspension was refluxed for 30 minutes and, after filtration over Celite, the solution was rotary evaporated. Gel permeation chromatography of the residue using toluene as the eluent afforded **9** as a greenish-blue solid (19 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.4–9.0 (3 m, 4H), 8.1–7.1 (5 m, 12H), 6.6 (m, 4H), 4.3–3.9 (m, 16H), 2.5–2.1 (m, 8H), 1.8–1.7 (m, 8H), 1.5–1.1 (m, 54H), 0.9–0.8 ppm (m, 15H). DEPT-^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 130.9, 130.5, 130.4, 130.3, 127.7, 126.0, 125.2, 124.0, 122.1, 117.2, 105.4, 100.6, 68.0, 68.0, 34.0, 29.9, 26.8, 25.0, 24.7, 22.9, 18.9, 14.9, 14.8, 14.8, 14.0, 14.0, 11.6. FTIR (KBr): ν (cm^{-1}) = 2962, 2919, 2850 (R-H), 1722, 1668, 1608, 1463, 1374, 1273, 1118, 1103, 727. UV-vis ($CHCl_3$): λ_{max} (nm) ($\log\varepsilon$ (dm^3 mol^{-1} cm^{-1})) = 650 (3.79), 598 (3.23), 362 (sh), 346 (3.67). MS (MALDI-TOF, DCTB), *m*/*z*: 1544–1550 $[M]^+$. HRMS: *m*/*z* = 1543.8604; calculated for $[C_{95}H_{121}N_9O_4SiZn]$: 1543.8597.

Tetraazaporphyrin 11

To a solution of **9** (18 mg, 0.012 mmol) in dry THF (2 mL), a TBAF solution (0.03 mL, 1 M in THF, 2.5 eq.) was added and the resulting solution was stirred at room temperature for 30 min. After addition of water (5 mL), the solution was extracted using DCM (2 × 5 mL). The organic phase was dried over Na_2SO_4, the solution was rotary evaporated, and the residue was dried. The resulting solid was transferred to a Schlenk tube, together with the thiadiazole **10** (6.1 mg, 1.5 eq.), $Pd(PPh_3)_4$ (0.67 mg, 0.01 eq.) and the mixture was deaerated. A deaerated benzene/triethylamine 1 : 1 solution (2 mL) was added, and the mixture was heated at 60 °C until all the starting material had reacted (4 h, monitored by TLC). After evaporation of the solvent at reduced pressure, water was added to the residue and the solution was extracted using CH_2Cl_2. The organic extracts were washed with water and brine and dried over $MgSO_4$. After evaporation of the solvent, gel permeation chromatography of the residue, using toluene as the eluent, afforded **11** (6 mg, 33%) as a greenish-blue solid. UV-vis ($CHCl_3$): λ_{max} (nm) ($\log\varepsilon$ (dm^3 mol^{-1} cm^{-1})) = 657 (3.79), 600 (sh), 441 (sh), 414 (sh), 344 (3.68). MS (MALDI-TOF, DCTB), *m*/*z*: 1656–1662 $[M]^+$.

Tetraazaporphyrin 12

To a solution of **11** (5 mg, 0.003 mmol) in a 3 : 2 mixture of THF/MeOH (2 mL), a solution of NaOH in water (1 mL, 20%) was added and the mixture was heated at 40 °C for 2 h. After cooling to rt, diethyl ether (5 mL) was added, and the solution was washed using HCl and water. The organic solution was dried ($MgSO_4$) and the solvent was rotary evaporated. The residue was chromatographed on silica gel using DCM, followed by a 1 : 99 mixture of MeOH/DCM, affording **12** (4 mg, 75%) as a green solid. FTIR (KBr): ν (cm^{-1}) = 2958, 2928, 2866 (R-H), 1726, 1716, 1683, 1668, 1558, 1456, 1374, 1230, 1064, 1038. UV-vis ($CHCl_3$): λ_{max} (nm) ($\log\varepsilon$ (dm^3 mol^{-1} cm^{-1})) = 650 (3.86), 600 (3.48), 4.52 (sh), 418 (sh), 346 (3.94). MS (MALDI-TOF, DCTB): *m*/*z* = 1642–1648 $[M]^+$. HRMS: *m*/*z* = 1641.7414; calculated for $[C_{99}H_{107}N_{11}O_6SiZn]$: 1641.7412.

Conclusions

A method to prepare ABAB-phthalocyanines and tetraazaporphyrin analogues, wherein A is a pyrrole or isoindole ring that can be substituted with a variety of functional groups, and the B-subunit consists of an isoindole ring functionalized with one iodine atom at the *meta*-position, has been developed. The procedure uses the crossover condensation of 5(6)-nitro-1,1,3-trichloroisoindolenine with a diiminopyrroline or diiminoisoindoline derivative as the key step, to assemble the ABAB macrocycle in a controlled fashion. The two nitro-functional groups are subsequently converted into iodo substituents in three synthetic steps. The manifold reactivity of iodo-substituents in different palladium catalyzed chemical transformations converts these diiodo-tetraazaporphyrins into valuable synthetic intermediates of ABAB- and ABAC-tetraazaporphyrins. As the B-subunit arises from a trichloroisoindolenine precursor that is unable to self-condense, the functionalization of the A-subunits is not conditioned to bulky moieties attached to the *ortho*-positions of isoindole rings. ABAB-phthalocyanines find applications in nonlinear-optics,[7d,30] the photodynamic inactivation of bacteria,[31] PDT,[32] organic field-effect transistors,[33] or as precursors of linear[34] and ladder polymers.[9b,35]

As a proof of concept, the controlled synthesis of a push–pull, ABAC dibenzoporphyrazine, containing a linear arrangement of the donor and acceptor fragments, has been prepared. This molecularly engineered phthalocyanine-type dye, which features the prototypical structure of a donor–π-bridge–acceptor, improves light-harvesting properties, and opens a route to push–pull phthalocyanine-like compounds of interest, for example, in DSSCs,[10a,21] electrocatalysis,[36] nonlinear optics,[37] or amphiphilic chromophores for biological applications.[38] We are currently applying the developed method to the preparation of regioisomerically pure compounds in related ABAC systems by examining the separation of regioisomers, in order to study their properties as photosensitizers in DSSCs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Financial support from Spanish MICINN (CTQ2017-85393-P, PID2020-116490GB-I00) is acknowledged. IMDEA Nanociencia acknowledges support from the ''Severo Ochoa'' Programme for Centres of Excellence in R&D (MINECO, Grant No. SEV2016-0686).

 This journal is © The Royal Society of Chemistry 2021

Published on 17 maio 2021. Downloaded on 07/10/2024 07:18:29.

DPM thanks "Convocatoria 617 – Doctorados en el exterior", COLCIENCIAS, Colombian government, for a doctoral fellowship.

Notes and references

1 J. Mack and N. Kobayashi, *Chem. Rev.*, 2011, **111**, 281–321.
2 V. N. Nemykin, S. V. Dudkin, F. Dumoulin, C. Hirel, A. G. Gürek and V. Ahsen, *ARKIVOC*, 2014, (i), 142–204.
3 For major reviews on the different procedures for the synthesis of tetraazaporphyrins and analogues see (*a*) M. S. Rodríguez-Morgade and T. Torres, 17.9.24 Phthalocyanines and Related Compounds, *Sci. Synth., Knowl. Updates*, 2017, **2**, 1–210; (*b*) N. B. McKeown, Product Class 9: Phthalocyanines and Related Compounds, *Sci. Synth.*, 2004, **17**, 1237–1368.
4 (*a*) T. G. Linßen and M. Hanack, *Chem. Ber.*, 1994, **127**, 2051–2057; (*b*) E. Fazio, J. Jaramillo-García, M. Medel, M. Urbani, M. Grätzel, M. K. Nazeerudin, G. de la Torre and T. Torres, *ChemistryOpen*, 2017, **6**, 121–127.
5 T. P. Forsyth, D. B. G. Williams, A. G. Montalban, C. L. Stern, A. G. M. Barrett and B. M. Hoffman, *J. Org. Chem.*, 1998, **63**, 331.
6 (*a*) S. Rodríguez-Morgade and M. Hanack, *Chem. – Eur. J.*, 1997, **3**, 1042–1050; (*b*) T. Fukuda, S. Homma and N. Kobayashi, *Chem. – Eur. J.*, 2005, **11**, 5205–5216.
7 (*a*) W. J. Youngblood, *J. Org. Chem.*, 2006, **71**, 3345–3356; (*b*) J.-D. Wang, M.-J. Lin, S.-F. Wu and Y. Lin, *J. Organomet. Chem.*, 2006, **691**, 5074–5076; (*c*) S. Dong, C. Bao, H. Tian, D. Yan, Y. Geng and F. Wang, *Adv. Mater.*, 2013, **25**, 1165–1169; (*d*) M. M. Ayhan, A. Singh, C. Hirel, A. G. Gürek, V. Ahsen, E. Jeanneau, I. Ledoux-Rak, J. Zyss, C. Andraud and Y. Bretonnière, *J. Am. Chem. Soc.*, 2012, **134**, 3655–3658; (*e*) M. M. Ayhan, A. Singh, E. Jeanneau, V. Ahsen, J. Zyss, I. Ledoux-Rak, A. Gül Gürek, C. Hirel, Y. Bretonniere and C. Andraud, *Inorg. Chem.*, 2014, **53**, 4359–4370; (*f*) M.-J. Lin and J.-D. Wang, *J. Mol. Struct.*, 2007, **837**, 284–289.
8 (*a*) M. Kandaz, S. L. Michel and B. M. Hoffman, *J. Porphyrins phthalocyanines*, 2003, **7**, 700–712; (*b*) S. B. Ekren, F. Dumoulin, E. Musluoglu, V. Ahsen and O. Guengoer, *J. Porphyrins phthalocyanines*, 2019, **23**, 1448–1454; (*c*) Y. Gök, H. Kantekin and İ. Değirmencioğlu, *Supramol. Chem.*, 2003, **15**, 335–343; (*d*) A. Altindala, Z. Z. Öztürk, S. Dabak and Ö. Bekaroğlu, *Sens. Actuators, B*, 2001, **77**, 389–394.
9 (*a*) M. M. Ayhan, Y. Zorlu, Ö. Gökdemir, A. Gül Gürek, F. Dumoulin, V. Ahsen and C. Hirel, *CrystEngComm*, 2014, **16**, 6556–6563; (*b*) M. Hanack and P. Stihler, *Eur. J. Org. Chem.*, 2000, 303–311.
10 (*a*) S. Yamamoto, S. Mori, P. Wagner, A. J. Mozer and M. Kimura, *Isr. J. Chem.*, 2016, **56**, 175–180; (*b*) N. Kobayashi, H. Miwa and V. N. Nemykin, *J. Am. Chem. Soc.*, 2002, **124**, 8007–8020.
11 F. Dumoulin, Y. Zorlu, M. M. Ayhan, C. Hirel, Ü. Isci and A. Ahsen, *J. Porphyrins phthalocyanines*, 2009, **13**, 161–165.
12 I. Aguirre de Carcer García, A. M. Sevim, A. de la Escosura and T. Torres, *Org. Biomol. Chem.*, 2013, **11**, 2237–2240.
13 H. Ali, S. Ait-Mohand, S. Gosselin, J. E. van Lier and B. Guérin, *J. Org. Chem.*, 2011, **76**, 1887–1890.
14 (*a*) W. Seitz, A. J. Jiménez, E. Carbonell, B. Grimm, M. S. Rodríguez-Morgade, D. M. Guldi and T. Torres, *Chem. Commun.*, 2010, **46**, 127–129; (*b*) A. J. Jiménez, M. Sekita, E. Caballero, M. L. Marcos, M. S. Rodríguez-Morgade, D. M. Guldi and T. Torres, *Chem. – Eur. J.*, 2013, **19**, 14506–14514.
15 H. Ali, O. St-Jean, J.-P. Tremblay-Morin and J. E. van Lier, *Tetrahedron Lett.*, 2006, **47**, 8275–8278.
16 M. Kloz, S. Pillai, G. Kodis, D. Gust, T. A. Moore, A. L. Moore, R. van Grondelle and J. T. M. Kennis, *J. Am. Chem. Soc.*, 2011, **133**, 7007–7015.
17 M. Ince, F. Cardinali, J.-H. Yum, M. V. Martínez-Díaz, M. K. Nazeeruddin, M. Grätzel and T. Torres, *Chem. – Eur. J.*, 2012, **18**, 6343–6348.
18 A. de la Escosura, M. V. Martínez-Díaz, D. M. Guldi and T. Torres, *J. Am. Chem. Soc.*, 2006, **128**, 4112–4118.
19 I. López-Duarte, M. Wang, R. Humphry-Baker, M. Ince, M. V. Martínez-Díaz, M. K. Nazeeruddin, T. Torres and M. Grätzel, *Angew. Chem., Int. Ed.*, 2012, **51**, 1895–1898.
20 W. M. Sharman and J. E. van Lier, *Synthesis of Phthalocyanine Precursors in The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, 2003, Vol. 15, pp. 45–47.
21 S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin and M. Grätzel, *Nat. Chem.*, 2014, **6**, 242–247.
22 H. Nie, A. G. M. Barrett and B. M. Hoffman, *J. Org. Chem.*, 1999, **64**, 6791–6796.
23 J. G. Young and W. Onyebuagu, *J. Org. Chem.*, 1990, **55**, 2155–2159.
24 The A4 macrocycle was only detected by MS of the reaction crude.
25 P. Stihler, B. Hauschel and M. Hanack, *Chem. Ber.*, 1997, **130**, 801–806.
26 (*a*) C. Yi, F. Giordano, N. L. Cevey-Ha, H. N. Tsao, S. M. Zakeeruddin and M. Grätzel, *ChemSusChem*, 2011, **4**, 591–594; (*b*) C. Yi, F. Giordano, N. L. Cevey-Ha, H. N. Tsao, S. M. Zakeeruddin and M. Grätzel, *ChemSusChem*, 2014, **7**, 1107–1113.
27 M. D. Hylarides, D. Scott Wilbur, S. W. Hadley and A. R. Fritzberg, *J. Organomet. Chem.*, 1989, **367**, 259–265.
28 Y. Rio, M. S. Rodríguez-Morgade and T. Torres, *Org. Biomol. Chem.*, 2008, **6**, 1877–1894.
29 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari,

A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision A.02*, Gaussian, Inc., Wallingford CT, 2009.

30 W. Cao, K. Wang, I. Ledoux-Rak and J. Jiang, *Inorg. Chem. Front.*, 2016, **3**, 1146–1151.

31 M. A. Revuelta-Maza, P. Gonzalez-Jimenez, C. Hally, M. Agut, S. Nonell, G. de la Torre and T. Torres, *Eur. J. Med. Chem.*, 2020, **187**, 111957.

32 M. A. Revuelta-Maza, M. Mascaraque, P. González-Jiménez, A. González-Camuñas, S. Nonell, Á. Juarranz, G. de la Torre and T. Torres, *Molecules*, 2020, **25**, 213.

33 S. Dong, C. Bao, H. Tian, D. Yan, Y. Geng and F. Wang, *Adv. Mater.*, 2013, **25**, 1165–1169.

34 A. Kumar Mutyala, S.-M. Hong, J. W. Namgoong, J. P. Kim and J. S. Park, *Dyes Pigm.*, 2017, **142**, 237–242.

35 (*a*) Y. Yamada, T. Kubota, M. Nishio and K. Tanaka, *J. Am. Chem. Soc.*, 2014, **136**, 6505–6509; (*b*) M. Suzuki, K. Yokota, H. Tsuchida, K. Yamoto, M. Nagata, S. Matsuoka, K. Takagi, K. Johmoto and H. Uekusa, *ACS Macro Lett.*, 2015, **4**, 247–250.

36 R. Nkhahle and T. Nyokong, *Electroanalysis*, 2021, **33**, 11–22.

37 A. Khadria, Y. de Coene, P. Gawel, C. Roche, K. Clays and H. L. Andersonm, *Org. Biomol. Chem.*, 2017, **15**, 947–956.

38 K. Zheng, X. Liu, H. Liu, D. Dong, L. Li, L. Jiang, M. Huang and C. Ding, *ACS Appl. Mater. Interfaces*, 2021, **13**, 10674–10688.

Published on 17 maio 2021. Downloaded on 07/10/2024 07:18:29.

 This journal is © The Royal Society of Chemistry 2021