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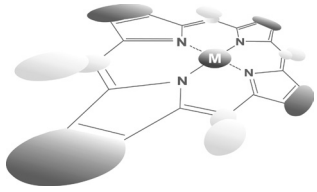

Synthesis and characterization of a β-fused tetraporphyrin-phthalocyanine star-shaped array

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Dedicated to Professor Tomás Torres on the occasion of his 65th birthday

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ABSTRACT: A star-shaped array, consisting in four tetraphenylporphyrin fused to a phthalocyanine central unit by pyrazine groups, is constructed *via* the condensation reaction of a dicyanoquinoxaline annulated to a porphyrin ring. The nature of the annulated group is critical for the success of the reaction; in the case of smaller linkers, such as a dicyanopyrazine unit, a nucleophilic substitution occurred, giving the corresponding alcoxy derivative in alcoholic solvents. The visible spectrum of the array shows the typical absorptions of the macrocyclic sub units. The synthetic pathway here presented opens the way to the preparation of β-fused porphyrin-phthalocyanine arrays.

KEYWORDS: porphyrins, phthalocyanines, chromophores.

INTRODUCTION

Porphyrin derivatives have been called the Pigments of Life [1], since their ubiquitous presence in biological materials imparts the color of the living systems. The impressive optical properties of porphyrins have led to an intense effort aimed to prepare synthetic mimics of the natural chromophores, with the aim to use them for applications in different fields, ranging from medicine to materials science [2]. Looking at the examples furnished by Nature, where even simple skeletal modifications induce important variations in the macrocycle properties, a cornucopia of different porphyrin analogs, *i.e.* macrocycles having framework modification to respect the parent porphyrin, have been prepared [3, 4]. Among them, phthalocyanines have a special role, rivalling that of porphyrins as the most famous and exploited pyrrolic macrocycles [5].

Even if the skeletal differences are relative small, with four aza moieties replacing, in the phthalocyanines, the *meso* methine bridges of porphyrins, they produce dramatic changes in the chemical and physical behavior of these macrocycles, with the optical properties being the most evident example.

Due to their expanded conjugated systems, all these compounds show intense absorptions in the visible region, but while porphyrins exhibit a strong Soret band around 410–450 nm, together with four weaker Q-bands around 500–600 nm, the aza-derivatives show lower absorptions at around 320–360 nm and quite intense ones at 600–700 nm. The photophysical as well as the redox properties of these classes of macrocycles are also very different, despite their structural similarity.

These differences, however, have also aroused the interest for the preparation of dyads or even arrays of macrocycles where these species are linked together through both their *meso*- and β-pyrrolic positions [6]. Most of the hybrids are linked either in a covalent manner or through a large metal center or even through electrostatic interactions, axial coordination, and other supramolecular interactions. The resulting hybrids can display the

◊ SPP full member in good standing

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complementary absorptions of individual chromophores, covering a large part of the visible spectrum; moreover, it is possible to exploit the interaction, when present, through photo-induced electron and/or energy transfer pathways. These systems are interesting in view of their unique photoelectronic properties and potential applications as mimics of light-harvesting systems in photosynthesis, as electron energy transfer moieties in molecular wires, as sensing materials and PDT [7–16].

Examples of porphyrin-phthalocyanine arrays have been reported in the literature, with different bridging units [17, 18]. In this field, we have been interested in the establishment of synthetic routes where two or more porphyrin units are annulated at their β-pyrrolic positions. In these compounds, the π-aromatic system is extended all over the molecules, resulting in significant changes in the UV-visible spectra, with new absorption bands featuring red shifts reaching the NIR region. In this pathway, we have reported the preparation of a star-shaped planar array, where four porphyrins were fused onto a central tetrabenzoporphyrin unit [19].

We have been interested to investigate the preparation of a similar system, where the central unit is a phthalocyanine ring. In this paper, we report a general method for the synthesis of dicyano porphyrinoid derivatives, and their potential application as precursors for the preparation of a more sophisticated architecture endowed with an extended aromatic system, based on a fused phthalocyanine-porphyrins oligomer.

EXPERIMENTAL

General

Silica gel 60 (70–230 mesh, Sigma Aldich) was used for column chromatography. Reagents and solvents (Aldrich, Merck or Fluka) were of the highest grade available and were used without further purification. ^{1}H NMR spectra were recorded on a Bruker AV300 (300 MHz) spectrometer. Chemical shifts are given in ppm relative to residual $CHCl_3$ (7.25 ppm). UV-visible spectra were measured on a Cary 50 spectrophotometer. Mass spectra were recorded on a VGQuattro spectrometer in the positive-ion mode, using *m*-nitrobenzyl alcohol (NBA, Aldrich) as a matrix (FAB), or on a Voyager DE STR Biospectrometry workstation in the positive mode, using α-cyano-4-hydroxycinnamic acid as a matrix (MALDI). Elemental analysis (C, H, N) were obtained at the Microanalytical Laboratory of the University of Padova, Italy.

Synthesis

Condensation reaction of Zn-dicyano porphyrin complex 1. Zn-dicyano porphyrin complex **1** (60 mg; 0.08 mmol) was dissolved in anhydrous pentanol, bubbled with nitrogen, and anhydrous $ZnCl_2$ (15 mg; 0.11 mmol) and a catalytic amount of DBU were added. The mixture was heated to reflux, under N_2, for 24 h, following the progress of the reaction by TLC analysis and UV-visible spectroscopy. After evaporation of the solvent, the crude product was purified on a silica gel chromatography column, eluting with dichloromethane. Only one fraction was isolated, collected and crystallized from dichloromethane/methanol, affording **2** (13 mg, 0.015 mmol; 21%); mp > 300 °C. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 406 (4.39), 440 (5.01), 565 (4.21), 604 (4.09). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 8.95 (m, 5 H, β-pyrroles), 8.83 (d, J = 4.77, 1 H, β-pyrroles), 8.22 (m, 4 H, phenyls), 8.09 (m, 4 H, phenyls), 7.79 (m, 4 H, phenyls), 4.10 (m, 2 H, –O–CH_2(CH$_2$)$_3$CH$_3$), 3.20 (m, 4 H, –O–CH$_2$(CH_2)$_3$CH$_3$), 1.79 (m, 2 H, –O–CH$_2$(CH_2)$_3$CH$_3$), 1.03 (m, 3 H, –O–CH$_2$(CH$_2$)$_3$CH_3). MS (FAB): *m/z* 841 [M]$^+$. Anal. calcd. for $C_{52}H_{37}N_7OZn$: C, 74.24; H, 4.43; N, 11.65. Found C, 74.47; H, 4.61; N, 11.10%.

Preparation of cyanopyrazinoporphyrin derivatives (compounds 4 and 5). Zn-dioxo-porphyrin complex **3** (80 mg; 0.11 mmol) was dissolved in a solution of dichloromethane/ethanol/acetic acid (5:5:1) (22 mL) and an excess of 4,5-diaminophthalonitrile (190 mg; 1.19 mmol) was added. The resulting solution was refluxed for 3 h, following the progress of the reaction by TLC analysis and UV-visible spectroscopy. After evaporation of the solvent, the crude product was purified on a silica gel chromatography column, eluting with dichloromethane. Two fractions were collected and crystallized from dichloromethane/methanol affording, in order of elution, porphyrin **5** (16 mg, 0.018 mmol; 16%) and **4** (56 mg, 0.068 mmol; 60%). **4.** mp > 300 °C. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 426 (5.41), 484 (4.63), 596 (4.07), 644 (3.92). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 8.97 (s, 4 H, β-pyrroles), 8.88 (s, 2 H, β-pyrroles), 8.48 (s, 2 H, quinoxaline), 8.22 (4 H, phenyls), 8.12 (4 H, phenyls), 7.96 (m, 2 H, phenyls), 7.80 (m, 10 H, phenyls). MS (FAB): *m/z* 884 [M]$^+$. Anal. calcd. for $C_{52}H_{28}N_8Zn$: C, 75.23; H, 3.40; N, 13.50. Found C, 75.45; H, 3.61; N, 12.10%. **5.** mp > 300 °C. UV-vis (CH_2Cl_2): λ_{max}, nm (log ε) 419 (5.57), 469 (4.85), 583 (4.27), 630 (4.19). ^{1}H NMR (300 MHz, $CDCl_3$): δ, ppm 8.95 (m, 4 H, β-pyrroles), 8.87 (s, 2 H, β-pyrroles), 8.38 (s, 1 H, quinoxaline), 8.28 (s, 1 H, quinoxaline), 8.22 (4 H, phenyls), 8.11 (4 H, phenyls), 7.93 (m, 2 H, phenyls), 7.80 (m, 10 H, phenyls). MS (FAB): *m/z* 831 [M]$^+$. Anal. calcd. for $C_{51}H_{28}BrN_7Zn$: C, 69.28; H, 3.19; N, 11.09. Found C, 68.91; H, 3.16; N, 11.73%.

Preparation of tetraporphyrinphthalocyanine 6. A suspension of magnesium turnings (175 mg, 7.2 mmol) in *n*-butanol (50 mL) was heated to reflux, under N_2, for 4 h using small crystal of iodine to initiate the reaction. Once cooled, this suspension was poured, under an atmosphere of nitrogen, into a flask containing the dicyanopirazino derivative **4** (40 mg, 0.057 mmol) and an excess of zinc acetate, and the mixture was heated again; finally, a catalytic amount of DBU was added and the mixture was

left to reflux, under nitrogen, for 24 h. The progress of the reaction was followed by TLC analysis and UV-visible spectroscopy. After evaporation of the solvent, the crude product was purified on a short column of silica gel eluting with tetrahydrofuran. The first fraction was isolated and characterized as the porphyrin **5** (9 mg, 0.0027 mmol; 5%). mp > 300 °C. UV-vis ($CHCl_3$): λ_{max}, nm (log ε) 425 (5.36), 584 (4.18), 622 (4.09), 833 (4.15). MS (MALDI): *m/z* 3385 $[M]^+$. Anal. calcd. for $C_{208}H_{112}N_{32}Zn_5$: C, 73.77; H, 3.33; N, 13.24. Found C, 74.25; H, 3.06; N, 12.94%.

X-ray crystallographic data

Diffraction data for **2** and **4** were collected at low temperature on a Nonius KappaCCD diffractometer with MoKα radiation and those for **5** on a Bruker Kappa Apex-II diffractometer equipped with CuKα radiation. Refinement was by full-matrix least squares using SHELXL, with H atoms in idealized positions, except for the OH hydrogen in **4**, for which coordinates were refined. **4** was the chloroform solvate, and **5** had disordered solvent of unknown identity, which was removed using SQUEEZE. **5** was also a two-component nonmerohedral twin and had substitutional disorder on adjacent C atoms in which CN and Br substituents overlap. Refinement of CN and Br occupancies summing to unity on each C led to values close to 50:50, consistent with mono CN monobromo formulation.

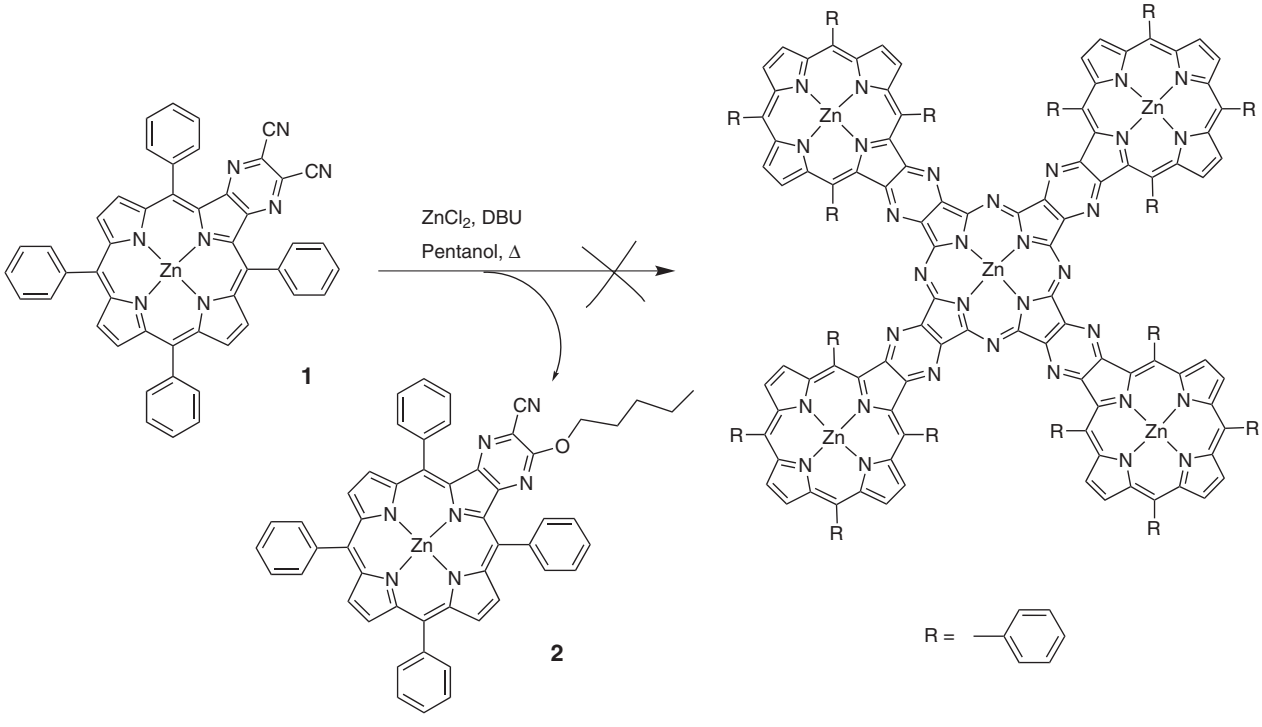
Crystallographic data. For **2.** $C_{53}H_{41}N_7O_2Zn$, monoclinic space group $P2_1/n$, a = 15.979(2), b = 20.040(4), c = 27.025(3) Å, β = 94.499(10)°, Z = 8, T = 90 K, D_{calcd} = 1.345 g.cm^{-3}, μ(MoKα) = 0.62 mm^{-1}. A total of 35,319 data was collected at to θ = 26.7°, R = 0.093 for 11,316 data with I>2σ(I) of 18,189 unique data and 1137 refined parameters, CCDC 1453163.

For **4.** $C_{53}H_{32}N_8OZn$. $CHCl_3$, triclinic space group P-1, a = 11.980(2), b = 13.447(3), c = 15.607(3) Å, α = 66.441(12), β = 72.978(13), γ = 82.031(11)°, Z = 2, T = 90 K, D_{calcd} = 1.480 g.cm^{-3}, μ(MoKα) = 0.79 mm^{-1}. A total of 30,184 data was collected at to θ = 25.7°, R = 0.054 for 5322 data with I>2σ(I) of 8382 unique data and 608 refined parameters, CCDC 1453164.

For **5.** $C_{52}H_{32}BrN_7OZn$, monoclinic space group P2/n, a = 21.1727(7), b = 10.9397(4), c = 21.7399(7) Å, β = 112.345(2)°, Z = 4, T = 90 K, D_{calcd} = 1.300 g.cm^{-3}, μ(CuKα) = 2.01 mm^{-1}. A total of 36,080 data was collected at to θ = 61.4°, R = 0.074 for 5580 data with I>2σ(I) of 7180 unique data and 588 refined parameters, CCDC 1453165.

RESULTS AND DISCUSSION

The synthetic pathway for the preparation of the target phthalocyanine-porphyrins array should start from a porphyrin bearing two vicinal cyanide groups in the peripheral positions. In the past, we have reported the preparation of a 2,3-dicyano-tetraphenylporphyrin, but all our attempts to obtain the corresponding phthalocyanine failed, probably due to the steric hindrance of the vicinal phenyl groups. To avoid this problem, we decided to prepare the dicyano porphyrin moiety **1**, as substrate in the self-condensation reaction leading to a heteroporphyrin-porphyrazine like structure (Scheme 1).



Scheme 1. Self-condensation reaction of **1**

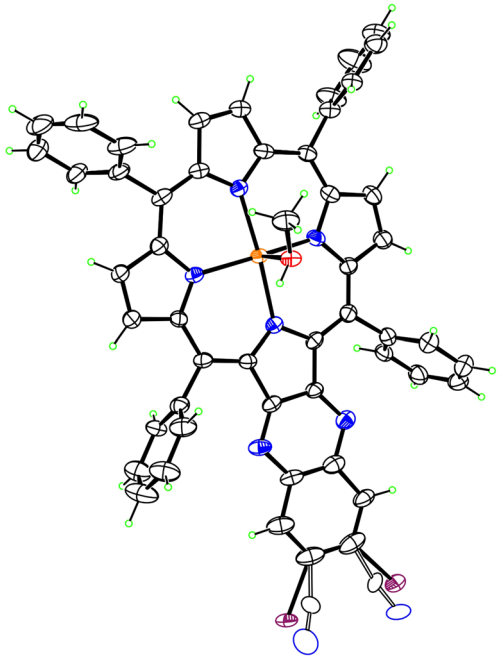


Fig. 1. X-ray crystal structure of **2** with 50% ellipsoids

The porphyrin **1** has been prepared by a condensation reaction of the Zn dioxoporphyrin with the diaminomaleonitrile, the synthesis of which was recently optimized in our laboratories [20]. This compound was reacted following a common procedure used for phthalocyanine preparation, by dissolving **1** in anhydrous pentanol, in presence of $ZnCl_2$ and DBU, and refluxing the mixture for 24 h. Chromatographic separation of the crude reaction mixture allowed the isolation of a reaction product. The UV-visible spectrum of this compound was quite similar to that of the starting material, showing the absence of the expected porphyrazine absorption, over 650 nm. This result indicated the failure to obtain the porphyrazine, while the retention of a single porphyrin structure suggested that reaction occurred on the peripheral pyrazine ring; the characterization of the compound highlighted the formation of the mono CN mono pentyloxyporphyrin **2**, confirmed by X-ray crystallography (Fig. 1).

The crystal of **2** has two independent molecules, one of which is shown. In both, the Zn is square pyramidal with a coordinated methanol in the axial position, mean Zn–O distance 2.174 Å, and the Zn lies 0.242 Å out of the plane of the four N atoms. The porphyrin cores exhibit a very slight saddle distortion, with the beta C atoms lying 0.024–0.269 Å (mean 0.112 Å) out of the N_4 plane.

The formation of **2** again indicated that the pyrazine ring is ineffective in avoiding the steric hindrance that can prevent the cyclization reaction leading to the porphyrazine ring; in this case the reactivity of the pyrazine ring toward nucleophilic aromatic substitution drives the reaction to the formation of **2**.

We next modified the reaction conditions, changing various parameters such as solvent, salt, catalyst or reaction time, as reported in Table 1. In all cases the reaction was not successful; in alcoholic media **1** always underwent the CN nucleophilic substitution, while in non-nucleophilic aromatic solvent, such as TCB or xylene, we observed no reaction, observing only the decomposition of the starting material.

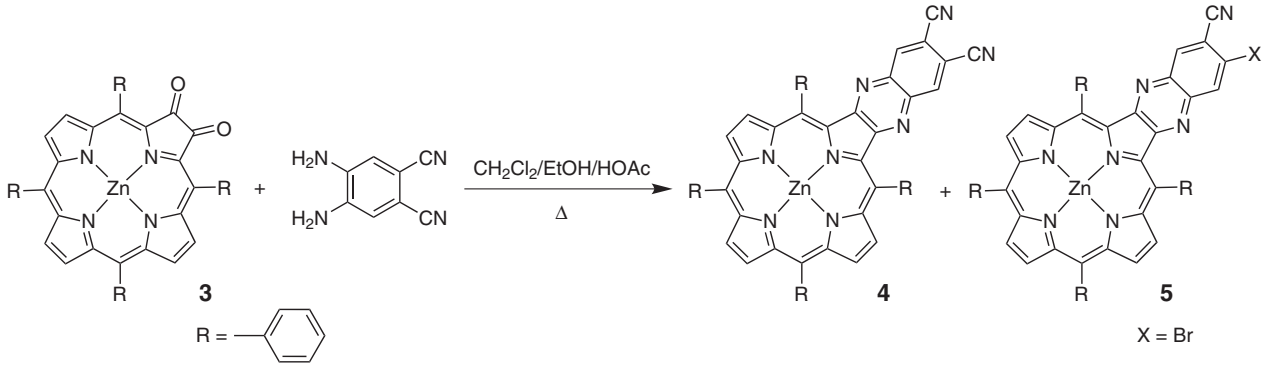
These results strongly support the hypothesis that the steric hindrance problem was not resolved, even in **1**, thus preventing the formation of the porphyrazine ring.

For this reason, we followed a similar approach, but modifying the reaction scheme starting from **3**, as illustrated in Scheme 2. In **4** the annulated ring is a quinoxaline, which allowed us to solve the two potential obstacles observed with **2**: the cyano groups are now substituents on a bezene ring, so more distant from the porphyrin ring and less activated toward the nucleophilic substitution.

Also in this case we obtained **4** by reaction of the dioxo porphyrin zinc complex **3**, with 1,2-diammino phthalonitrile,

Table 1. The products obtained from the reaction of the porphyrin **1** in different conditions

Starting material	Solvent	Salt	Cat.	Reaction time	Product
1	pentanol anhydrous	$Zn(OAc)_2$	DBU	24 h	**2**
1	hexanol anhydrous	$Zn(OAc)_2$	DBU	24 h	mono-substituted
1	hexanol anhydrous	$ZnCl_2$	DBU	24 h	mono-substituted
1	Mg/I_2 butanol	$Zn(OAc)_2$	DBU	24 h	mono-substituted
1	1,2,4-trichlorobenzene	$Zn(OAc)_2$	DBU	48 h	—
1	DMF	$ZnCl_2$	HMDS	48 h	—
1	Xylene	$Zn(OAc)_2$	HMDS	48 h	—



Scheme 2. The formation of **4** and **5** from the reaction of porphyrin **3**

in a EtOH/CH_2Cl_2/CH_3CO_2H solvent mixture, refluxing for 3 h. Once TLC showed the disappearance of the starting material, the solvent was removed and the residue was purified by column chromatography on silica gel, eluting with CH_2Cl_2; in this case we obtained two fractions, in 60% and 16% yield, respectively (Scheme 2).

Although their UV-visible spectra were very similar, slightly shifted by only a few nanometers, the ^{1}H NMR analysis revealed a different substitution pattern for the porphyrin derivatives. The second fraction, identified as the desired product **4**, shows a singlet around 8.5 ppm, integrating for 2 H, which correspond to the residual protons of the quinoxaline ring. The presence of only one signal corroborated the formation of the expected symmetric derivative. Lower symmetry was observed in the ^{1}H NMR spectrum of the first fraction. In detail, the signal corresponding to quinoxaline protons splitted into two (1 H each) resonances, and also the signals of the β-pyrroles signals increased in number.

Both these features suggested that a substitution occurred in the peripheral quinoxalino group, as suggested also by the corresponding mass spectra.

For both compounds we have been able to obtain crystals suitable for X-ray crystallographic characterization, which allowed us to unambiguously identify the products. Compound **4** (Fig. 3) was the expected compound, while the additional product **5** was a similar quinoxalino fused-porphyrin, where one cyano group and a bromine atom were present at the peripheral positions (Fig. 4).

The structure of **4** is quite similar to that of **2**, with the Zn lying 0.241 Å out of the N_4 plane and the Zn–O(MeOH) distance 2.146 Å. The saddle distortion is slightly more pronounced than in **2**, with beta C atoms 0.099–0.276 (mean 0.182) Å out of the N_4 plane. The structure of **5** has disorder in which the adjacent Br and CN positions are swapped. The Zn coordination is similar to that seen in **2** and **4**, with the Zn lying 0.226 Å out of the N_4 plane and the Zn–O distance 2.189 Å. The porphyrin core is somethat more planar than those **2** and **4**, with the 24 atoms lying a mean of 0.053 Å from coplanarity and the maximum deviation of a beta C atom 0.123 Å.

The formation of **5** was quite surprising, since no bromine sources have been employed in preparation of the porphyrin derivative. For this reason we turned our attention toward the commercial 4,5-diaminophthalonitrile used as starting material. The synthetic route for the preparation of the 4,5-diaminophthalonitrile uses dibromo-diaminobenzene as intermediate and a mono Br-mono CN diamino benzene was present as an impurity in the commercial reagent used, as confirmed by HPLC separation and mass analysis of the reagent. Probably this impurity is more reactive than the corresponding 4,5-diaminophthalonitrile, and only the excess of phthalonitrile led to the formation of **5** in appreciable amount.

The desired dicyano-porphyrin **4** was then reacted, following the synthetic route based on the preliminary preparation of $Mg(OBu)_2$, in refluxing butanol, with Mg and I_2. After 4 h, the solvent was poured in a flask containing **4** and $Zn(OAc)_2$ and a catalytic amount of DBU was added. The mixture was heated to reflux, under nitrogen, for 24 h. The progress of the reaction was monitored by TLC and UV-visible spectroscopy; in this case the UV-visible spectrum showed a significant peak around 840 nm, together with some modifications of the starting porphyrin absorptions, suggesting the formation of a phthalocyanine like structure **6** (Scheme 3), further supported by the red-shift of the peak.

The work up of the reaction was particularly difficult, since the low solubility showed by **6** in several organic solvents made it difficult to purify the crude reaction product; furthermore, the reaction yields were quite low, making more difficult the separation of the pure product. The strong tendency of the compound to aggregate led also to a very broad ^{1}H NMR spectrum.

The identification of the compound was also supported by the MALDI mass spectrum, which was in agreement with the structure of **6**.

The UV-visible spectrum of **6** is presented in Fig. 5; it is worth mentioning that the spectrum seems to be the sum of the characteristic absorbances of both porphyrins and phthalocyanine, and only a broadening and red shift can be observed. This feature seems to indicate minimal

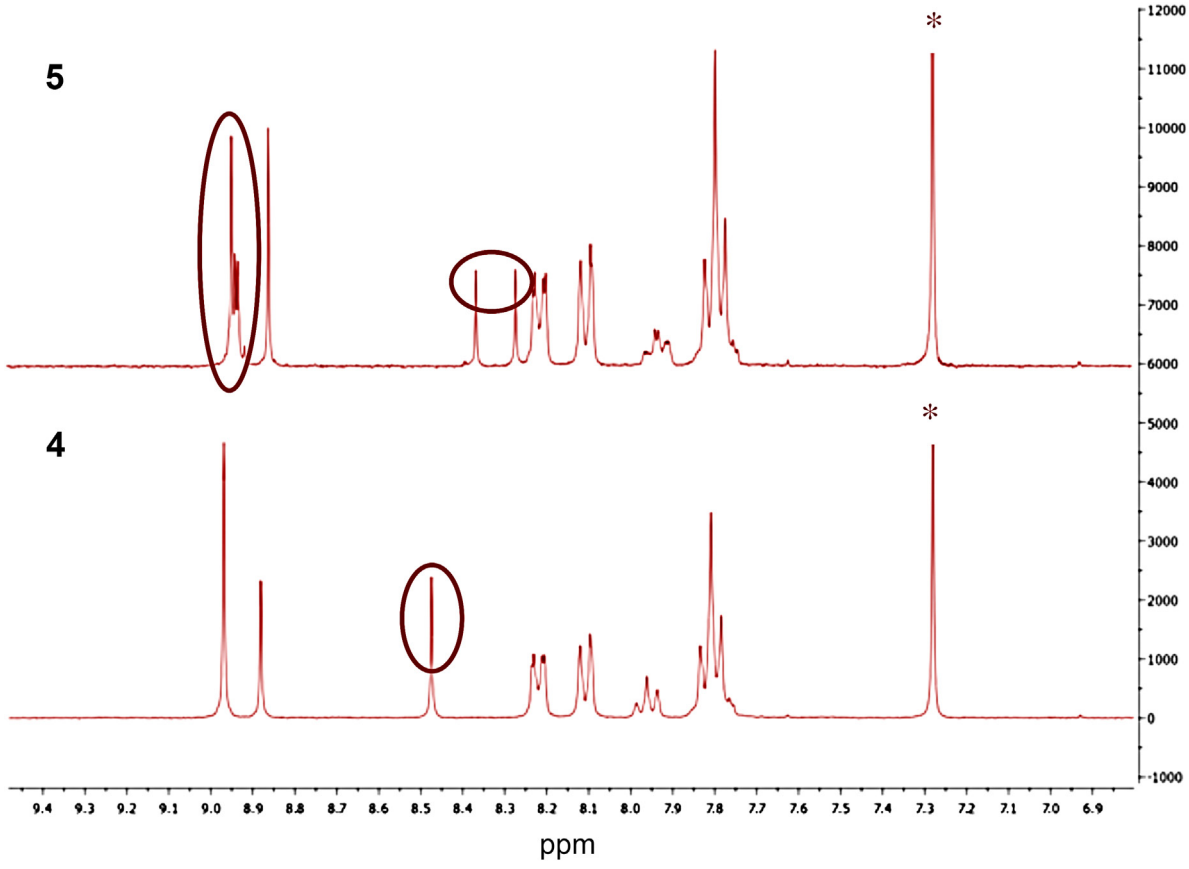


Fig. 2. ^{1}H NMR spectra of compounds **4** and **5** in $CDCl_3$. The asterisk indicates the residual solvent peak

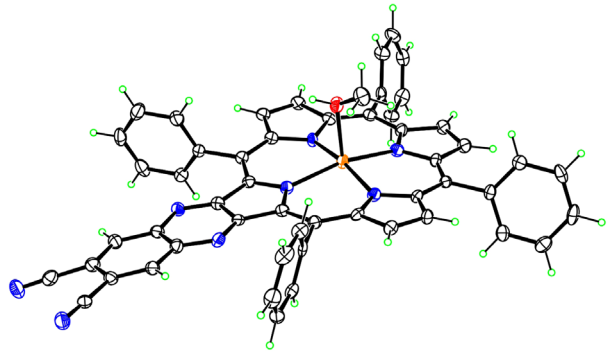


Fig. 3. X-ray crystal structure of **4** with 50% ellipsoids

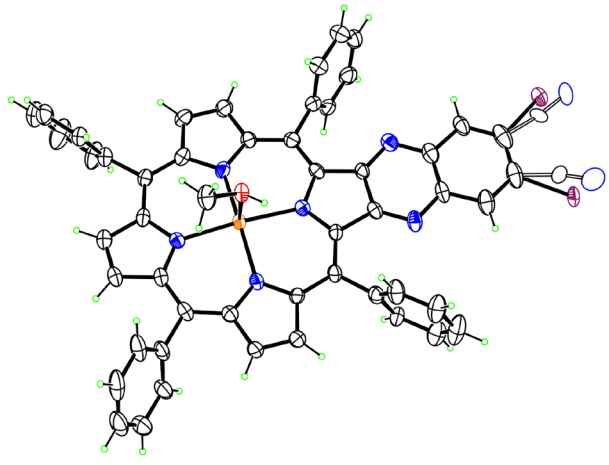
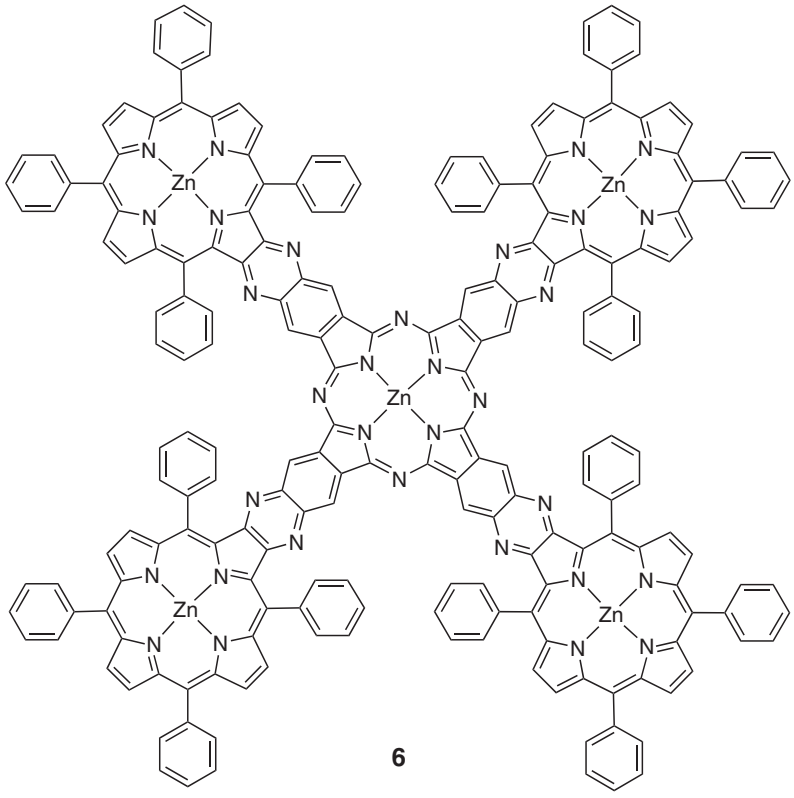


Fig. 4. X-ray crystal structure of **5** with 50% ellipsoids, illustrating the disorder of the Br and CN substituents

interactions between the aromatic systems of the five tetrapyrrolic subunits. It is interesting to note that the UV-visible spectrum of **6** was significantly influenced by the solvent used. In Fig. 5a we show the spectrum obtained in $CHCl_3$, which confirms the strong tendency of **6** to aggregate. The addition of pyridine, in fact, induced a modification of the spectrum, as indicated in Fig. 5a, with a better resolution of the bands. In this case, the coordination of pyridine can in fact reduce intermolecular aggregation. This effect is even more evident when the spectrum is measured in a coordinating solvent, such as the THF (Fig. 5b).

In conclusion, we have established a suitable synthetic procedure for the preparation of β-fused porphyrin-phthalocyanine array. The star shaped array **6** shows a strong tendency toward aggregation, which is a serious drawback for a complete characterization



Scheme 3. Structure of **6**

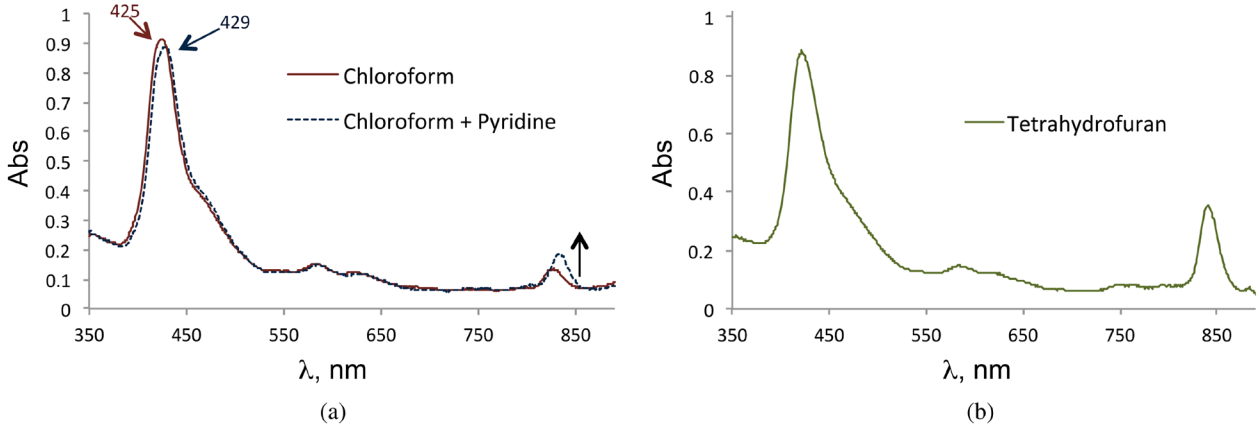


Fig. 5. UV-visible spectra of **6** in (a) $CHCl_3$ (full line), $CHCl_3$ + pyridine (dotted line) and (b) THF

of the properties of the compound. However it should be noted that this problem can be significantly reduced by a judicious choice of the *meso*-aryl groups of the porphyrin subunits, and these studies are now ongoing in our laboratories.

Supporting information

^{1}H NMR spectra for **2**, **4** and **5** and mass spectra of **2**, **4**, **5** and **6** (Figs S1–S7) are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center (CCDC) under numbers CCDC-1453163, CCDC-1453164, CCDC-1453165. Copies can be obtained on request, free of charge, *via* www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: data_request@ccdc.cam.ac.uk).

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