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Multiply biphenyl substituted zinc(II) porphyrin and phthalocyanine as components for molecular materials

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In memory of Christian G. Claessens

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ABSTRACT: The preparation and physico-chemical characteristics of zinc(II) porphyrin and phthalocyanine derivatives with biphenyl units are reported. These compounds have been prepared as components for molecular electronics systems and rotor-based molecular machines, where the biphenyl units can act as paddles because they are oriented quasi-perpendicularly to the plane of the aromatic macrocycles which would be coordianted through the transition metal ion by an axial ligand. The minimalist design along with the absence of solubilizing groups leads to a low solubility of the compounds in organic solvents; the phthalocyanines is only sparingly soluble while the porphyrin is more easily manipulated, but in any case the concentration of both compounds is sufficient for surface deposition. The luminescence of the compounds is characteristic of the central unit, although it is clear in the absorption spectra that the phthalocyanine derivative has a particularly strong tendency to aggregate non-specifically. The porphyrin forms microcrystals while the phthalocyanines which bears eight biphenyl units forms amorphous aggregates from 1,2-dichlorobenzene reminiscent of glasses of other biphenyl derivatives, which is interesting for the preparation of amorphous materials for optics applications.

KEYWORDS: aromatic compounds, organic dyes, π-functional materials, molecular electronics.

INTRODUCTION

The search for novel molecular materials which might have utility in areas such as molecular electronics [1–7], photovoltaic current generation [8–12], and even molecular machines [13–19] is leading many researchers to explore the synthesis and self-assembly of complex compounds containing π-functional units — among them porphyrins and phthalocyanines — which are often at the heart of their function [20–26]. Yet simplicity and symmetry are often attractive features which lead to excellent solid state properties because of the lack of dilution of the π-functional units by solubilizing groups, even if the solubility of these apparently simple compounds can limit processing possibilities [27]. We were attracted to 4-substituted biphenyl derivatives [28–36] of π-functional units because these groups are well-defined spatially (that is, their general calamitic shape points in a certain direction determined by their connectivity) and they might aid in electrical or mechanical transmission of energy. Rubrene is an inspiration to us in this sense, insofar as it contains phenyl substituents attached to an essentially flat aromatic core to which they are oriented perpendicularly [37]. Although intuition might suggest that the conformation

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◊SPP full member in good standing

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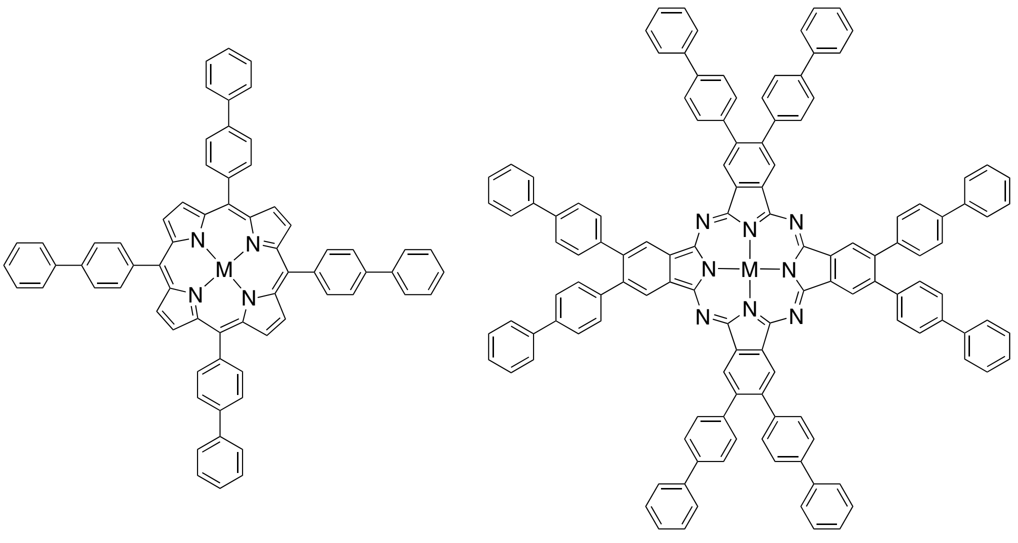


1 M = 2H
Zn1 M = Zn

2 M = 2H
Zn2 M = Zn

Formulae

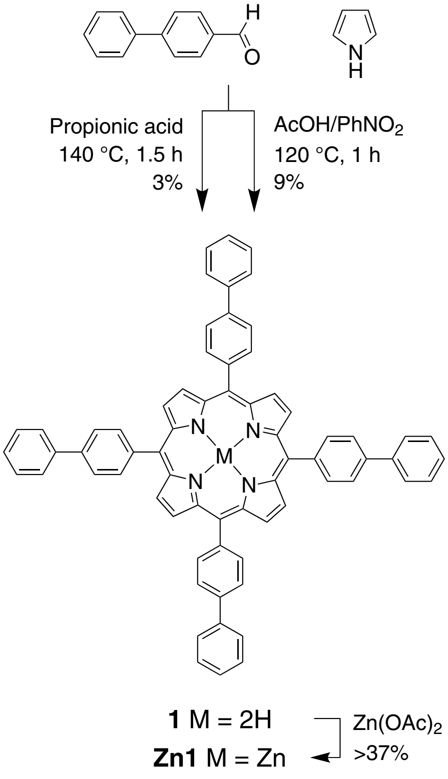
of these groups could hinder charge transport, rubrene has excellent electronic properties [38].

Porphyrins and phthalocyanines are π-functional units that have proven interest as photoconductors [39], components of photovoltaic devices [40–42], and in molecular electronics in general [43–48]. In addition, their C_4 symmetries are appealing for both solid state packing and for components for rotors when the central metal atom is coordinated orthogonally to the plane of the macrocyclic ring. Here we report the preparation of derivatives of these cores with biphenyl units joined directly to them. The porphyrin **1** and phthalocyanine **2** and their zinc(II) complexes (**Zn1** and **Zn2**) have been synthesized, fully characterised, their tendency to form aggregates has been studied, and their photochemical characteristics established.

RESULTS AND DISCUSSION

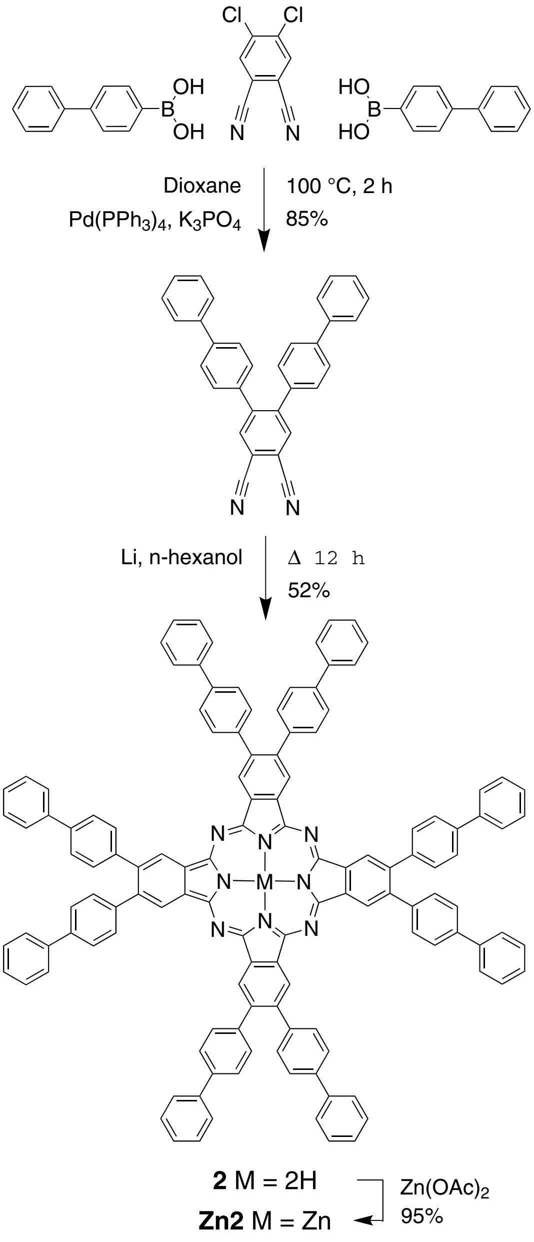
Synthesis and characterisation

The porphyrin and phthalocyanine derivatives **1** and **2** were prepared by the synthetic routes shown in Schemes 1 and 2. The porphyrin (Scheme 1) was obtained by reaction of biphenyl-4-carboxaldehyde with pyrrole either under the classic conditions in boiling propionic acid in air or by heating in a mixture of acetic acid and nitrobenzene [49], with a very recent report using the BF_3 etherate method [50]. Having assayed the former two methods, that in acetic acid and nitrobenzene proved to be more effective and substantially easier to work up, in accord with the cited procedure [49], although the yield reported previously could not be reproduced. The great advantage of this procedure is that the resulting porphyrin crystallizes directly from the cooled reaction mixture. The crystals were washed with EtOH in order to remove traces of nitrobenzene, to give an overall yield of 9%, compared with a reported 12% for the BF_3 etherate method [50].



1 M = 2H
Zn1 M = Zn

Scheme 1.



Scheme 2.

While the mass and IR spectra of **1** are in total accord with its structure, the ^{1}H NMR spectrum of the porphyrin (at 300 MHz in $CDCl_3$ at a concentration of 1.16×10^{-2} M and at room temperature) exhibits broad signals of very low intensity compared with that expected given the concentration. Increasing the temperature at which the spectrum was recorded only achieved a marginal improvement. Addition of 1.5% CF_3COOD by volume to the $CDCl_3$ solution (which results in deuteration of the basic pyrrolic nitrogen atoms) causes a clear improvement in the intensity and resolution of the signals as well as a slight shift of some of the resonances (Fig. 1). These observations could be a result of aggregation of the porphyrins under these experimental conditions, presumably favored by the biphenyl substituents present on the porphyrin periphery since tetraphenyl porphyrins do not usually show this behavior. Addition of acid causes the protonation of the porphyrin, which becomes positively charged and adopts a distorted rather than planar structure, so that the electrostatic repulsion disfavors aggregation and aids solubilization. As a consequence, the ^{1}H NMR signals are sharp and well-defined.

In order to confirm this hypothesis, we tested if aggregation was concentration dependent. To check concentration dependency, we prepared a set of samples of compound **1** ranging from 7 mM to 0.1 mM. From the spectra recorded it can be concluded that when concentration diminishes a progressive reduction of the broadness, was observed, and the appearance, initially weakly, of the well-defined aromatics signals (Fig. 2). There is not a continuous shift of the signals, rather a very broad signal appears centred at approximately 7.5 ppm at high concentrations, which indicative of a rapid aggregation of non-specific interactions caused by the poor solubility rather than a particular strong non-covalent interaction. It is conceivable that the biphenyl units could enter into edge-on interactions which lead to this aggregation.

Incorporation of zinc(II) into the centre of **1** to give the new zinc(II) complex proved surprisingly difficult. The usual method for preparing the metallated porphyrin in dichloromethane [51–54] only resulted in partial metallation of the sample, in spite of the large excesses of $Zn(OAc)_2$ added (up to 16 equivalents) and the long reaction times used (up to 76 h). Absorption spectroscopy and laser desorption-ionization time of flight (LDI-TOF) mass spectrometry both indicated the presence of starting material. We surmise that the high tendency of **1** to aggregate in the solvent is at least partially responsible for the poor efficiency of the reaction under these conditions. Subsequently the solvent was changed to *N*,*N*-dimethylformamide, in order to give more energy to the reaction by increasing the temperature (to 153 °C), and because of the greater solubility of $Zn(OAc)_2$ that is insoluble in CH_2Cl_2 (although this is not usually an impediment). The reaction time and the number of equivalents of $Zn(OAc)_2$ required were not optimized, but no more starting material was found in the reaction mixture after 24 h as indicated by LDI-TOF MS. The complete inclusion was also evidenced by the absence of the N–H band in the IR spectrum, as well as the characteristic (UV-vis) absorption spectrum (*vide infra*).

The phthalocyanine **2** was prepared in two steps from 4-biphenylboronic acid and 4,5-dichlorophthalonitrile using palladium tetrakis(triphenylphosphine) as coupling reagent (Scheme 2). The intermediate 1,2-dicyano-4,5-bis-biphenylbenzene showed the characteristic spectroscopic signals expected for this kind of compound in the NMR spectrum, especially the singlet at 7.92 ppm corresponding to the protons in the central phenyl ring, as well as the CN band in the IR spectrum at 2229 cm^{-1}. Formation of the phthalocyanine from this dinitrile proceeded smoothly by reacting it with lithium in hexanol. The

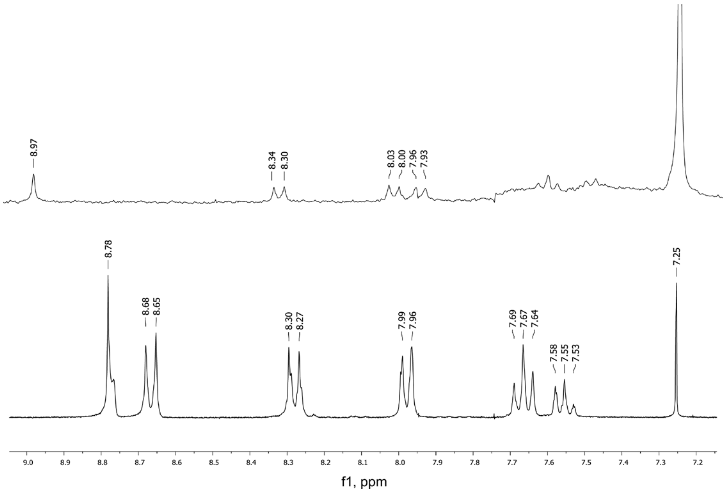


Fig. 1. ^{1}H NMR spectra of **1** in $CDCl_3$ at a concentration of 1.16×10^{-2} M and at room temperature (top) and below in $CDCl_3/CF_3COOD$ (98.5/1.5) under otherwise identical conditions. The peak at $\delta = 7.25$ ppm corresponds to the residual signal of chloroform in $CDCl_3$

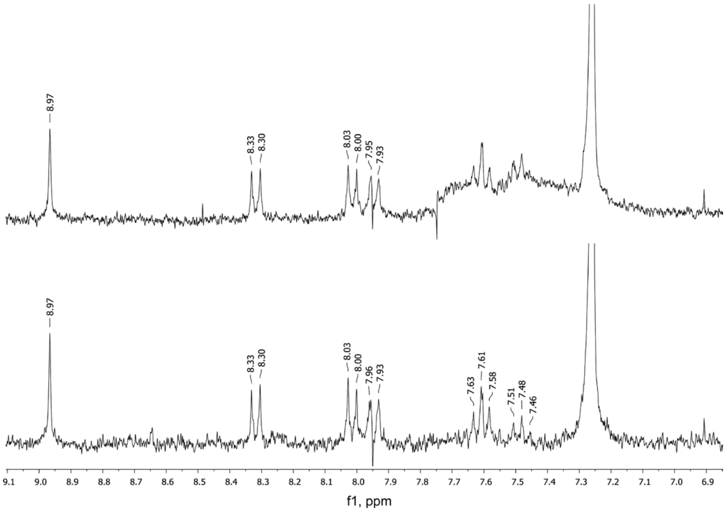


Fig. 2. ^{1}H NMR spectra (300 MHz) in $CDCl_3$ of compound **1** at two different concentrations: 7 mM (top), and 0.1 mM (bottom). The peak at $\delta = 7.25$ ppm corresponds to the residual signal of chloroform in $CDCl_3$

product was purified by repeated washings with acetic acid, methanol, and dichloromethane. Compound **2** is a green microcrystalline powder that is largely insoluble in all common solvents at room temperature. We could not identify a solvent which permitted recording of the ^{1}H NMR spectrum of the molecule. The LDI-TOF mass spectrum of **2** clearly indicates the authenticity of the compound. The characteristic (UV-vis) absorption bands of the free base phthalocyanine are observed clearly, although a broad band corresponding to an aggregate was present. The preparation of the zinc(II) phthalocyanine was successfully achieved by heating the free base compound with an excess of zinc(II) acetate. Curiously, no difficulties were encountered in the incorporation of the metal ion despite the apparently strong tendency of the molecules to aggregate, in apparent contradiction to the observations made for the porphyrin but which is an empirical fact. The product does not show better solubility than its free base precursor, but the absorption and LDI-TOF spectra confirm its identity.

Optical microscopy of solids

In order to investigate the capacity of the compounds to form ordered solid state materials which might be interesting for opto-electronic applications, the porphyrins and phthalocyanines were precipitated from solution. The porphyrins can be dissolved in hot chloroform, toluene and dioxane, and crystallized upon cooling. The largest and most well–defined solid was obtained from chloroform from which rhombic crystals precipitate (Fig. 3 for compound **1**). The crystals have well-defined edges in the main, and are clearly birefringent when observed with a polariser at different angles with respect to the sample. The crystals also show the fluorescence characteristic of the porphyrins in the solid state. When the porphyrins were crystallised from either dioxane or toluene (in which they are slightly less soluble than in chloroform) smaller and less well-defined crystallites were formed.

The solubilization of the phthalocyanines **2** and **Zn2** is considerably more challenging than the biphenyl-substituted porphyrins. The only solvent found which provided sufficient solubility of these compounds in order to attempt a crystallisation process was 1,2-dichlorobenzene. The compounds were apparently well-dissolved near the boiling point of the solvent, but when the solutions were allowed to cool a flocculent apparent solid was observed at the solvent-air interface. When the suspension was cast onto glass and was observed with a polarising optical microscope, blobs of amorphous material containing very small crystallites were observed. Figure 4 shows one of these regions, wherein the amorphous majority of the material has solid lumps with sizes below 5 μm in all cases.

Photochemical characterisation

The absorption spectra of the porphyrins show the two characteristic bands, one at around 420 nm (Soret band, with an extinction coefficient ε around 10^5 $M^{-1}.cm^{-1}$) and less intense bands between 500 and 650 nm (Q-bands, with lower extinction coefficient values of *ca*, 10^3-10^4 $M^{-1}.cm^{-1}$) [55, 56]. The Soret band of **1** is located at *ca.* 422 nm ($S_0 \rightarrow S_2$ transition), and is red-shifted by 1 nm in the Zn(II) complex. The four less intense Q-bands ($S_0 \rightarrow S_1$ transition) are observed at 517, 554, 593 and 647 nm for the free-base porphyrin, at virtually identical positions for other tetraaryl porphyrins [57–59]. The

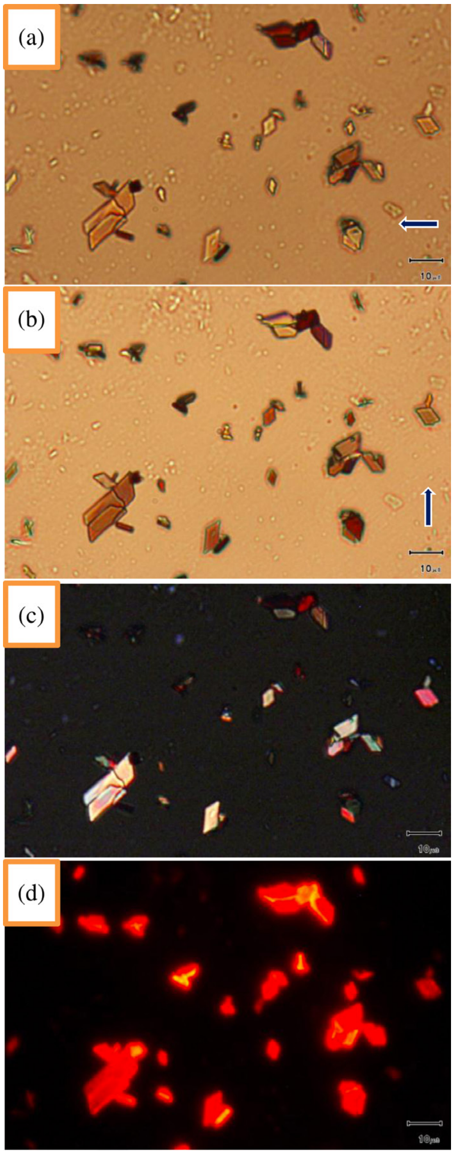


Fig. 3. Optical microscope images of **1** crystallized from chloroform, A and B transmission images with a bottom polarizer at the positions indicated by the arrows above the scale bar, C is a transmission image with crossed polarisers, and D is a reflection fluorescence image with GFP filter. In all cases the scale bar corresponds to 10 μm

lowest energy bands disappear for the metalloporphyrins and this lower number of electronic absorption bands is attributed to an increase in the molecular symmetry upon complex formation (the protons in the free base porphyrin are localised on the timescale of the spectroscopy). Additionally, an absorption band is observed with maximum at 254 nm corresponding to the π–π* transitions associated with the phenyl groups (pendant "arms") of the porphyrins.

Excitation of diluted dichloromethane solutions of compounds **1** and **Zn1** results in the characteristic porphyrin emission bands. The emission spectra were recorded at 298 K and at 77 K. Two bands were observed

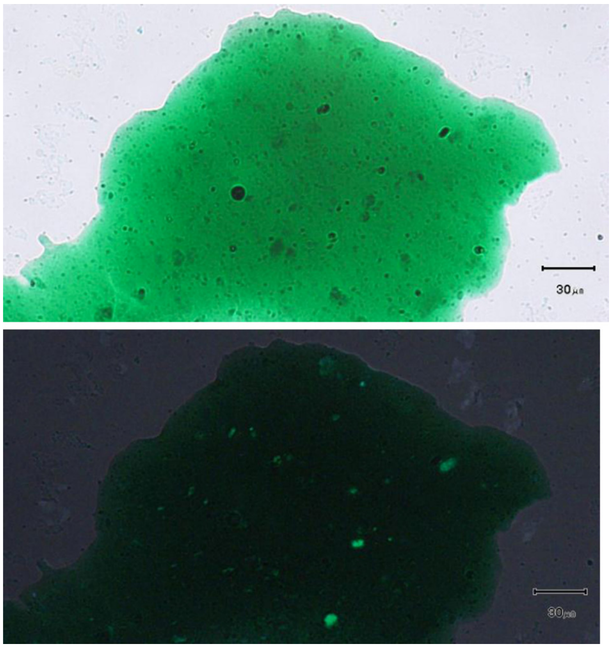


Fig. 4. Transmission optical microscope images of **2** precipitated from 1,2-dichlorobenzene, top image with parallel polarizers and bottom image with crossed polarizers. The scale bars corresponds to 30 μm

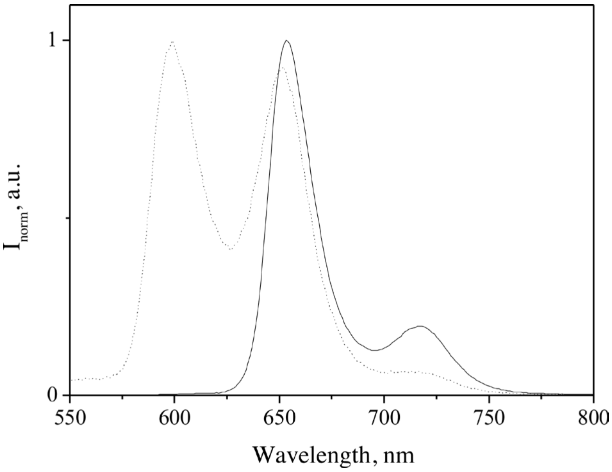


Fig. 5. Normalized emission spectra of **1** (solid line) and **Zn1** (dotted line) in dichloromethane solution at 1 × 10^{-6} M (298 K)

in the red region which are weaker and blue-shifted for the metalloporphyrin with respect to the free-base system (Fig. 5). The emission spectra are dominated by $S_1 \rightarrow S_0$ fluorescence [60]. The shorter-wavelength feature is the Q(0,0) band and the longer-wavelength feature is the Q(0,1) vibronic satellite (Table 1). The same emission was observed when the samples were excited at the Soret and the different Q-bands. The lowest energy emission band increases in intensity for the metallated porphyrins. No emission was observed in any case when the samples were excited in the phenyl absorption band. Low temperature experiments (77 K)

Table 1. Absorption and emission data of the free-base porphyrin and phthalocyanine and their corresponding Zn(II)-complexes at 1×10^{-6} M and at 298 K (in dichloromethane for **1** and **Zn1** and THF for **2** and **Zn2**)

Compounds	Absorption maximum nm ($\varepsilon \times 10^{-3}$, $M^{-1}.cm^{-1}$)	Emission maximum nm (298 K)	τ (singlet, ns)	Φ	k_r ($\times 10^{-6}$, s^{-1})	k_{nr} ($\times 10^{-6}$, s^{-1})
1	254 (119.2), 422 (531.2), 517 (27.3), 554 (23.4), 593 (17.6), 647 (20.3)	654, 717	5.36	0.079	14.7	172
Zn1	247 (138.2), 423 (496.9), 547 (37.9), 587 (26.1)	599, 652	1.72	0.037	21.5	560
2	686, 717*	723, 761, 808	3.80	0.065	24.9	355
Zn2	695*	700, 721sh, 776	2.63	0.043	11.4	252

*The absorption coefficients are not given for these compounds because of the high state of aggregation makes it impossible to attain a reliable value.

resulted in the same emission bands which were slightly sharper than the room temperature spectra. The excitation collected at both emission maxima match well with the corresponding absorption spectrum, which proves the involvement of the porphyrin ring at the origin of the emission (Fig. 6).

Solid-state experiments displayed broad emissions one order of magnitude lower in intensity than those recorded in solution for the free ligands and non-emissive metallated derivatives. This effect arises from concentration quenching, as reported for similar derivatives [54, 55].

In an attempt to analyze in more detail the characteristics of the emission processes, the fluorescence lifetimes were measured in solution. The time-correlated single photon counting technique was used upon excitation of the samples at 370 nm and the results are summarized in Table 1. The recorded lifetime of the metallated compound is shorter than that of the free-base molecule because of the heavy metal effect, i.e. metallation of the porphyrin quenches the fluorescence. The fluorescence quantum yield of the free-base compound **1** is also about the double than the corresponding to the metallated species **Zn1**. (Table 1).

Radiative, k_r, and non-radiative k_{nr}, decay constants (Table 1) were calculated assuming that the emissive state is formed with unitary efficiency in each case when excited directly into the porphyrins at 420 nm and taking into account that:

$$k_r = \Phi / \tau \text{ and } k_{nr} = 1/\tau - k_r$$

It is observed that non-radiative constants (k_{nr}) are one order of magnitude higher than the corresponding k_r, as observed in other porphyrins [61].

The absorption spectra of the free-base phthalocyanine **2** and the corresponding zinc(II)-complex were recorded in THF at a concentration 1×10^{-6} M and the results are summarized in Table 1. The absorption spectra of both compounds are poorly resolved. The Soret (~370 nm) and the Q-bands (~690 and 715 nm) could be identified and are in the expected regions for these compounds [62–66] although they are buried under broad transitions, characteristic of the presence of aggregated phthalocyanines [62–67].

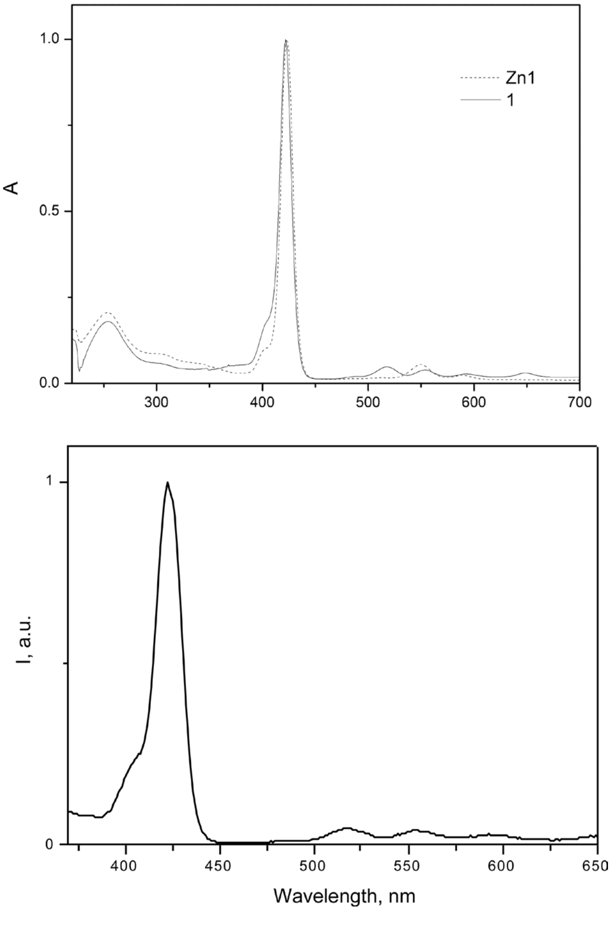


Fig. 6. Absorption spectra of **1** and **2** (top) and normalized excitation spectrum of **1** in dichloromethane solution (bottom, 1×10^{-6} M, $\lambda_{em} = 422$ nm)

The phthalocyanine compounds are not very soluble in most solvents but THF seemed to be a good choice since the increased solvent polarity improved the spectral resolution. This solvent proved to be a good candidate in other works [62–66]. Decreasing the concentration did not eliminate aggregates, and a very broad absorption

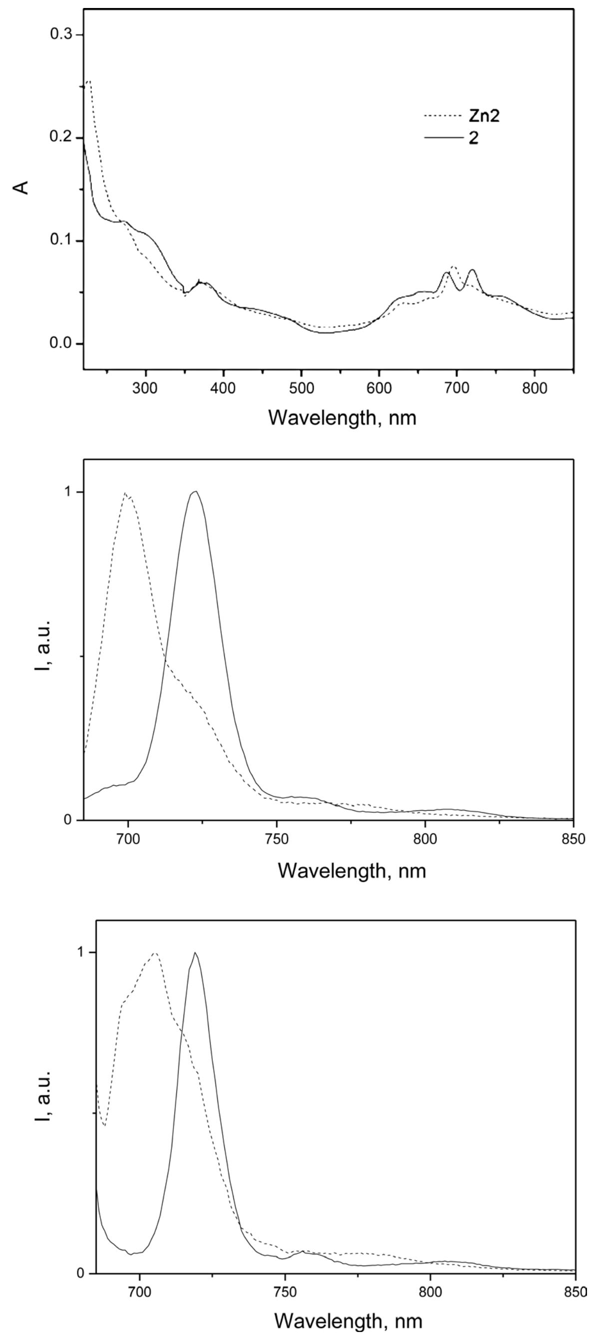


Fig. 7. Absorption spectra of the phthalocyanines (top) and normalized emission spectra of **2** (solid line) and **Zn2** (dashed line) in approximately 1 × 10^{-6} M THF solution at room temperature (middle) and at 77 K (bottom). λ_{exc} = 680 nm

band persisted even at very low concentration. Emission spectra were recorded in *ca.* 1 × 10^{-6} M THF solutions at RT and 77 K (λ_{exc} = 680 nm, Fig. 7). A very intense emission band is observed for both compounds, with clear maxima located at 723 and 700 nm (with a shoulder at *ca*. 720 nm) for the free base phthalocyanine and for the metal-complex respectively. As observed with the porphyrins, the emission of the zinc(II)-derivative is blue-shifted with respect to its metal-free parent. Emission experiments at 77 K display similar features, although the shoulder around 720 nm observed in the metallic compound increases in intensity (Fig. 7).

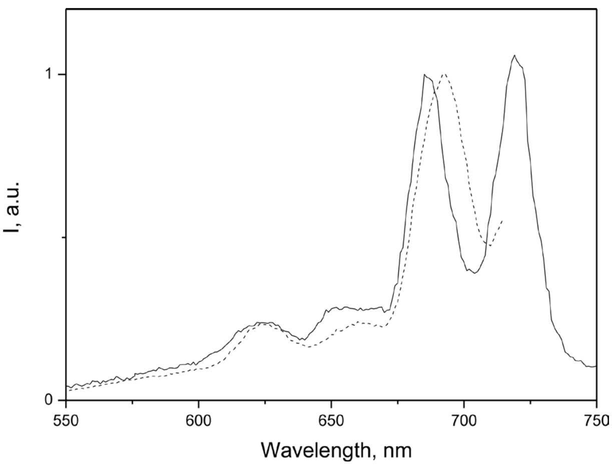


Fig. 8. Normalized excitation spectra of **2** (solid line, λ_{em} = 762 nm) and **Zn2** (dashed line, λ_{em} = 723 nm) in approximately 1 × 10^{-6} M THF solution

The excitation spectra reproduce the absorption spectra of the molecules without the broad aggregate band observed in the absorption spectra. This observation indicates that the species responsible for the emission are the isolated solvated molecules (Fig. 8).

Fluorescence quantum yields are summarized in Table 1. The lifetime is in the order of 2–4 ns as observed for other similar complexes [65] and is shorter for **Zn2** than for **2**, which could be due to the heavy atom effect as in the case of the porphyrins. As there, the k_{nr} constant is one order of magnitude greater for the metallic complex.

CONCLUSION

The synthesis of oligo-biphenyl derivatives of zinc(II) porphyrin and phthalocyanines has been achieved with relative ease, and although the compounds show the expected low solubility in organic solvents, they are sufficiently dispersed to allow the characterisation of their photophysical properties and the concentration levels will allow the study of their binding and adsorption to surfaces. The processing of the phthalocyanines product is a particular challenge at the present time, presumably because of the increased number of biphenyl units and the intrinsically lower solubility of phthalocyanines when compared with tetraaryl porphyrins, and the surface assembly of this compound is an attractive prospect, since surface-based rotors are an area of great interest [68–69], and although the solubility is low it is sufficient to allow surface deposition.

It is remarkable that the phthalocyanines does not seem to precipitate from solution, but forms a disordered state, similar to layers of oligoethyleneoxide-substituted phthalocyanines on mica [70] which in turn reminds us of layers of porphyrins on the same surface [71, 72]. The bulk disordered state requires further investigation, but some biphenyl derivatives do show glass-like behavior [73]. We are presently exploring these possibilities, because the amorphous state can be advantageous for optics applications.

EXPERIMENTAL

General

The starting materials were purchased commercially and were used without further purification. Thin-layer chromatography (TLC) was performed on aluminium plates coated with Merck Silica gel 60 F254. Developed plates were air-dried and scrutinized under a UV lamp. Silica gel 60 (35–70 mesh, SDS) was used for column chromatography. Mass spectrometry was performed on a LC/MSD-TOF mass spectrometer from Agilent Technologies. The samples were deposited directly onto a non-polished stainless steel sample plate from solution. ^{1}H and ^{13}C NMR spectra were recorded using the deuterated solvent as lock and tetramethylsilane as internal reference.

Photophysical experiments

Absorption spectra were recorded on a Cary 100 scan 388 Varian UV spectrometer at 298 K and fluorescence emission spectra on a Horiba-Jobin-Yvon SPEX Nanolog-TM at 298 K and 77 K. The values of quantum yield were determined at 298 K with respect to $[Ru(bipy)_3]Cl_2$ in water as standard reference ($\Phi = 0.042$) [74]. The fluorescence decays were obtained using a home-built equipment that has been described elsewhere [75] and were analyzed using the method of modulating functions implemented by Striker *et al*. [76] and on an Edinburgh Instruments LifeSpec-II spectrometer based on the time correlated single photon counting (TCSPC) technique, equipped with a PMT detector, double subtractive monochromator and 635 nm picosecond pulsed diode lasers source as excitation (decay fittings were done with F900 software from Edinburgh Instruments).

Synthesis

5,10,15,20-tetrakis(4-biphenyl)porphyrin (1). Method A. Propionic acid (14 mL) was heated to reflux, then pyrrole (190 μL, 2.74 mmol) and biphenyl-4-carboxaldehyde (0.5 g, 2.74 mmol) were added, all in air. The solution became dark immediately. After 1.5 h the reaction was allowed to cool down and was filtered. The solid was dissolved in CH_2Cl_2 and extracted with a solution of 10% Na_2CO_3 in H_2O (2 × 15 mL). The organic phase was evaporated under reduced pressure and the crude product purified by column chromatography (CH_2Cl_2/EtOAc 95:5) to give 1 as a purple solid (75 mg, 3%). mp > 350 °C. ^{1}H NMR (300 MHz, $CDCl_3$/CF_3COOD (98.5/1.5), 25 °C): δ, ppm 8.78 (s, 8H, pyr.), 8.67 (d, *J* = 9 Hz, 8H, $H_{2,6}$), 8.29 (d, *J* = 9 Hz, 8H, $H_{3,5}$), 7.98 (d, *J* = 6 Hz, 8H, $H_{2',6'}$), 7.67 (t, *J* = 6 Hz, 8H, $H_{3',5'}$), 7.55 (t, *J* = 6 Hz, 4H, $H_{4'}$). MS (LDI TOF): *m/z* 919.2 calcd. for $(C_{68}H_{46}N_4)^+$ 918.3 $[M]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm 423, 518, 554, 593, 649. IR (ATR): ν, cm^{-1} 3317 (NH). Elemental analysis; found C, 88.60; H, 5.32; N, 6.34, expected C, 88.86; H, 5.04; N, 6.10. **Method B.** A mixture of acetic acid (20 mL) and nitrobenzene (15 mL) was heated to reflux, then pyrrole (190 μL, 2.74 mmol) and biphenyl-4-carboxaldehyde (0.5 g, 2.74 mmol) were added, all in air. The solution became dark immediately. After 1 hour, the reaction was cooled down and filtered, and the crystals that had formed were washed with EtOH (3 × 8 mL) to give 4 as a purple solid (0.215 g, 8.5%). The sample was characterized as for method A.

Zinc(II) 5,10,15,20-tetrakis(4-biphenyl)porphyrin (Zn1). Method A. A solution of **1** (95 mg, 0.1 mmol) in CH_2Cl_2 (28 mL) was heated to reflux under an argon atmosphere. $Zn(OAc)_2$ (64 mg, 0.4 mmol) dissolved in a 1:1 mixture of MeOH (9 mL) and CH_2Cl_2 (9 mL) was added dropwise, and the whole was refluxed for 72 h. The mixture was extracted with a saturated solution of $NaHCO_3$ (2 × 15 mL) and brine (2 × 15 mL). The organic phase was evaporated under reduced pressure and the crude product purified by column chromatography (CH_2Cl_2/EtOAc 95:5) to give **Zn1** as a purple solid (51 mg, 52%). mp > 350 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ, ppm 9.07 (s, 8H, pyr.), 8.31–7.45 (m, 36H, arom.). MS (LDI TOF): *m/z* 982.5 calcd. for $(C_{68}H_{44}N_4Zn)^+$ 982.4 $[M]^+$. UV-vis (CH_2Cl_2): λ_{max}, nm 426, 552, 594. Elemental analysis; found C, 82.88; H, 4.79; N, 5.87, expected C, 83.13; H, 4.51; N, 5.70. **Method B.** A solution of **1** (100 mg, 0.109 mmol) in DMF (30 mL) was heated to reflux under an argon atmosphere. $Zn(OAc)_2$ (68 mg, 0.435 mmol) dissolved in DMF (20 mL) was added dropwise and the whole was refluxed for 24 h. Then the DMF was evaporated and CH_2Cl_2 (50 mL) was added. The solution was extracted with a saturated solution of $NaHCO_3$ (2 × 15 mL) and brine (2 × 15 mL). The organic phase was evaporated under reduced pressure and the crude product purified by washing with acetone (3 × 8 mL) to give **8** as a purple solid (40 mg, 37%); the sample was characterized as for method A.

1,2-dicyano-4,5-bis(4-biphenyl)benzene. A mixture of 4,5-dichlorophthalonitrile (500 mg, 1.52 mmol), 4-biphenylboronic acid (663 mg, 3.35 mmol) and palladium tetrakis(triphenylphosphine) (116 mg) in dioxane (15 mL) was combined with K_3PO_4 (2.12 g, 10 mmol) in water (4 mL) under nitrogen and the whole was heated at 100 °C for 2 h. The product was purified by column chromatography on silica gel using ethyl acetate-hexane as eluent, yielding the pure compound as a white solid (55 mg, 85%). The solid was crystallised from chloroform-hexane to afford the product as transparent colourless crystals which are fluorescent. MS (LDI TOF): *m/z* 432.4 calcd. for $(C_{32}H_{20}N_2)^-$ 432.2 $[M]^-$. ^{1}H NMR (250 MHz, $CDCl_3$): δ, ppm 7.92 (s, 2H), 7.65–7.55 (m, 8H), 7.53–7.36 (m, 6H), 7.27 (d, 4H). ^{13}C NMR (63 MHz, $CDCl_3$): δ, ppm 145.8, 141.8, 140.2, 136.9, 136.0, 130.3, 129.3, 128.3, 127.7, 127.4, 115.9, 114.8. IR (ATR): ν,

cm^{-1} 3032 (w), 2229 (w, CN), 1601 (m), 1589 (m), 1480 (m), 1447 (w), 1406 (w), 1366 (w), 1269 (w), 1190 (w), 1114 (w), 1075 (w), 1006 (w), 923 (m), 841 (s), 769 (s), 734.5 (s), 698 (s). Elemental analysis; found C, 88.74; H, 4.73; N, 6.53, expected C, 88.86; H, 4.66; N, 6.48.

2,3,9,10,16,17,23,24-octakis(4-biphenyl) phthalocyanine (2). Under an argon atmosphere, hexanol (260 μL) and lithium metal (3.7 mg, 0.53 mmol) were stirred for 2 h at 100 °C to generate lithium hexanoate. 1,2-dicyano-4,5-bis(4-biphenyl)-benzene (100 mg, 0.23 mmol) was added as a solid and the mixture was heated at 160 °C for 12 h. Glacial acetic acid (5 mL) was added, and the mixture was filtered and washed with acetic acid (5 mL), methanol (10 mL) and dichloromethane (20 mL). The solid was boiled in toluene and filtered three times, and then washed with dichloromethane to leave a deep green solid 52%. mp > 350 °C. MS (LDI TOF): *m/z* 1730.8 calcd. for $(C_{128}H_{82}N_8)^+$ 1730.7 $[M]^+$. UV-vis (THF): λ_{max}, nm 686, 717. Elemental analysis; found C, 88.93; H, 4.77; N, 6.30, expected C, 88.76; H, 4.77; N, 6.47.

2,3,9,10,16,17,23,24-octakis(4-biphenyl) phthalocyaninatozinc(II) (Zn2). Phthalocyanine **2** (18 mg, 10 μmol) was suspended in DMF with a large excess of zinc(II) acetate (32 mg, 0.2 mmol) and the mixture was stirred at 100 °C for 24 hours under argon. Once at room temperature, the mixture was filtered and the solid was washed sequentially with water, acetonitrile, ethyl acetate, and chloroform; then, it was dried in vacuum, to give **Zn2** in 95% yield. mp > 350 °C. MS (LDI TOF): *m/z* 1793.6 calcd. for $(C_{128}H_{80}N_8Zn)^+$ 1793.1 $[M]^+$. UV-vis (THF): λ_{max}, nm 695. Elemental analysis; found C, 85.24; H, 4.67; N, 6.02, expected C, 85.63; H, 4.49; N, 6.24.

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