Modulating the electronic properties of porphyrinoids: a voyage from the violet to the infrared regions of the electromagnetic spectrum

Yannick Rio, M. Salomé Rodríguez-Morgade* and Tomás Torres*

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This paper examines the preparation of tailor-made azaporphyrins and analogues exhibiting their Q-bands in several particular and predetermined regions of the electromagnetic spectrum. The applications of phthalocyanines, the possibility of preparing novel related porphyrinoids with different colour properties and, consequently, new emerging applications, are discussed.

1. Introduction

It is well known that colours result from light. The interaction between an object and an incident light determines how a human observer perceives that object. Colour is the visual sensation produced by the light that an object reflects with wavelengths within the so-called visible range. The sensation of violet colour is produced by low wavelength radiation—around 380–450 nm—whereas a red colour is the consequence of higher wavelength radiation—625–780 nm. These colours are the limits of the visible spectrum, which is flanked by the ultraviolet and infrared zones. Intermediate wavelengths produce blue, green, yellow and orange colours. The colours that we are able to see are due to the selective absorption of light by means of chemical compounds—pigments—or physical phenomena. For instance phthalocyanines, the main protagonists of this article, absorb in the red and therefore they have blue–green colours.

Nowadays, colours play an extremely important role not only in science and technology, but also in our everyday lives. The technological applications of colour chemistry are expanding in areas such as photonics, electro-, thermo- and photochromic devices, electroluminescence, colour displays, holography, photosensitizers, photodynamic therapy, data storage, solar cells, and light emitting diodes, among many others.[1]

2. The electronic properties of porphyrinoid macrocycles

Conjugated tetrapyrrolic macrocycles like porphyrin derivatives constitute ideal structures to be used as absorbers in a wide region of the electromagnetic spectrum. In fact, nowadays it is possible to obtain a porphyrinoid-based structure absorbing in any region of the visible spectrum. The reason for such versatility arises from the chemical structure of such macrocycles, and especially the numerous modifications that may be performed on them, giving rise to a great assortment of compounds. Therefore, the name "porphyrin" (**1**, Fig. 1) was first applied to a class of naturally occurring, deep red or purple pigments sharing a large aromatic

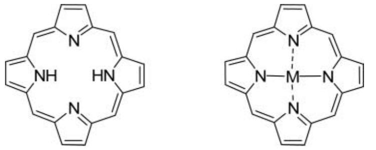


Fig. 1 The basic skeleton of a porphyrin (**1**) as a free-base and as a metal complex.

Departamento de Química Orgánica, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain. E-mail: tomas.torres@uam.es, salome.rodriguez@uam.es; Fax: +34-91-4973966; Tel: +34-91-4974151 (T. Torres); Tel: +34-91-4974707 (M. S. Rodriguez-Morgade)

Tomás Torres, M. Salomé Rodríguez-Morgade and Yannick Rio (left to right)

Yannick Rio *studied chemistry at University Louis Pasteur, Strasbourg. His PhD was supervised by Dr J.-F. Nierengarten and Prof. J.-F. Nicoud (IPCMS, Strasbourg). From 2003 to 2005 he worked at the laboratory ISOF (Bologna, Dr Nicola Armaroli). In 2005 he joined Prof. Torres' group at UAM. His current research focus is the synthesis of new phthalocyanine, boron dipyrrin and dipyrromethane derivatives.*

M. Salomé Rodríguez-Morgade *received her PhD at UAM in 1995. She spent a year as a postdoctoral fellow with Prof. Michael Hanack at the University of Tübingen, Germany, then two years as a "Marie Curie" research fellow in Prof. Anthony Barrett's group at Imperial College, London. In 1999 she joined Prof. Torres' group at UAM and since 2003 has held a "Ramón y Cajal" research contract.*

Tomás Torres *is Professor of Organic Chemistry at the Autónoma University of Madrid (UAM). His research interests include the study of the physical properties of molecular materials based on phthalocyanines. His group is exploring several areas of application, including organic and hybrid solar cells, with a focus on nanotechnology. Prof. Torres is the author or co-author of* ca. *280 papers, reviews and patents.*

ring formed by four pyrrole rings that are bound together through four methylene bridges (*meso* carbons). This kind of arrangement produces a flat macrocyclic molecule, whose superior properties cannot be deduced from those of its parts. However, the name "porphyrin" is currently associated with a variety of macrocycles of different composition and size that display a huge number of different physicochemical properties and applications.[2]

The optical properties of the porphyrins constitute some of their most fascinating attributes. Thus, their UV–vis spectra consist of two absorptions in two different regions, like other aromatic compounds such as benzene itself. What makes these compounds so special is the fact that these absorption bands appear in the near-ultraviolet and in the visible regions, respectively. Porphyrins display an intense band at 390–425 nm, called a B- or Soret band, and between two and four weaker bands appearing at 480–700 nm (Q-bands). The exact location, number and intensity of these bands strongly depend upon the substitution pattern of the macrocycles as well as whether the porphyrin is metallated or not and the kind of metal coordinated by the central cavity. Hence, free-base porphyrins show four Q-bands (IV, III, II and I, Fig. 2a) with different relative intensities, depending on the functionalization both at the β-pyrrole positions and the *meso* carbons, so that the spectra are classified as *etio-type*, *rhodo-type*, *oxo-rhodo-type* or *phyllo-type*. Protonation of porphyrins produces a more symmetrical ring, thus simplifying the spectrum by Q-band collapse from four to two bands. Metallation of the macrocycle also gives rise to spectra displaying only two Q-bands, denoted as α- (appearing at lower energy) and β- (Fig. 2b). The relative intensities of these two bands are intimately related to the kind of metal used and its coordination mode. Metalloporphyrins are also catalogued as "regular" or "irregular", producing *normal*, *hypso* or *hyper* electronic spectra, respectively. All these modifications of the UV–vis spectrum occur very often with variation in the position of the B-band and with concomitant colour change.

Although there have been many attempts to justify the main aspects of the porphyrin UV–vis spectrum through detailed theoretical calculations, Martin Gouterman and co-workers were the first to successfully interpret the electronic spectrum of the porphyrins by means of theoretical concepts.[3,4] The so-called four-orbital model postulated by Gouterman uses the two HOMOs and LUMOs generated by simple Hückel theory[5] so that the frontier orbitals of the basic porphyrin macrocycle are related to the e_4 and e_5 orbital levels of a 16- or 18-membered cyclic polyene. In porphyrin complexes the symmetry is reduced to D_{4h}. The transitions from the two HOMOs, namely the $1a_{1u}$ and $1a_{2u}$, and the doubly degenerated LUMO, which is the $1e_g{}^*$ orbital, account for the typical spectrum of porphyrins (Fig. 3). Gouterman assumed that the $1a_{1u}$ and $1a_{2u}$ HOMOs are accidentally degenerated for porphyrin complexes, despite the reduction of the symmetry to D_{4h} with respect to the inner cyclic polyene. As a result, the B- and Q-transitions almost completely retain their allowed and forbidden characters, with respect to the corresponding 18 π-electron cyclic polyene. In this situation, the B-band is the dominant spectral feature since it is allowed. The Q-bands are forbidden. The fact that they exist is because of molecular vibrations within the porphyrin ring, which make them weakly allowed. However, perturbation of the structure can result in the lifting of this degeneracy for the HOMO orbitals,

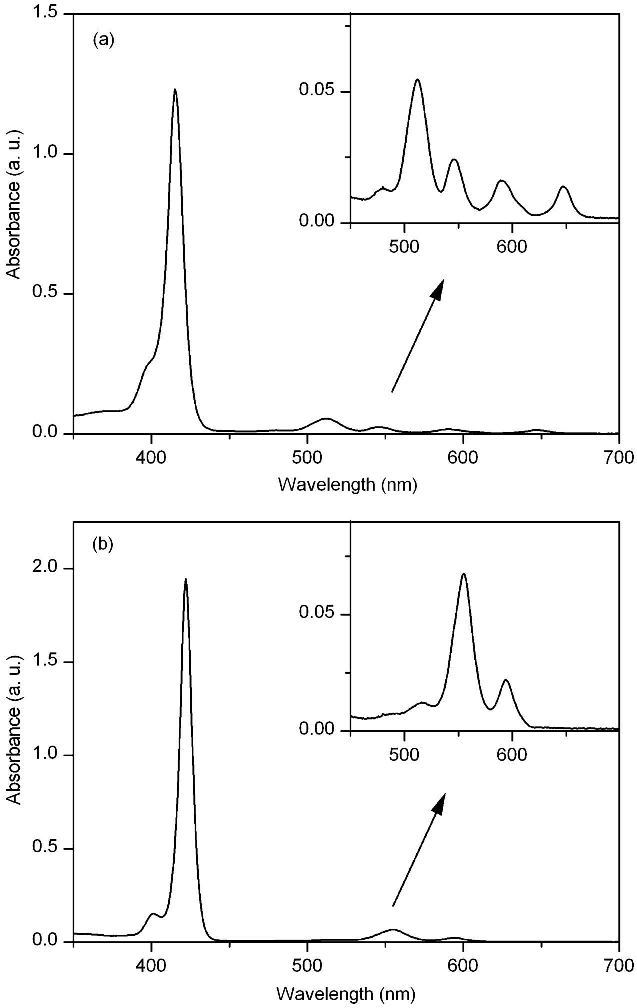


Fig. 2 Typical UV–vis spectra for (a) a free-base porphyrin and (b) a porphyrin–metal complex.

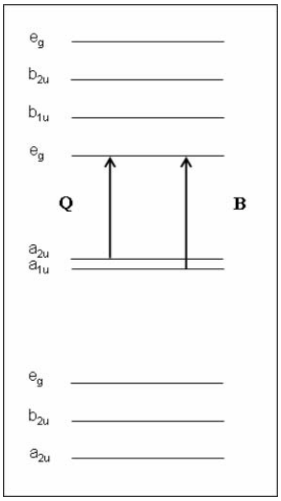


Fig. 3 The scheme of energy levels in metallated porphyrins with the first two $\pi \rightarrow \pi^*$ transitions, the Q- and B-bands, marked.

giving rise to spectra with different features to those typical of porphyrins. With this or other purposes in mind, the porphyrin molecule can be moulded and adapted to different applications by simple modification of its basic skeleton. Therefore, porphyrins can be functionalized with groups of different nature at either or both of the β-pyrrole positions or at the *meso* carbons.

Concerning structural changes, the formal introduction of heteroatoms (nitrogen) at the four *meso* positions of the *porphyrin* basic structure (**1** in Fig. 1) affords the *porphyrazines*[6] (section 4), whereas the condensation of four benzene rings onto the pyrrol units gives rise to *tetrabenzoporphyrins*. The introduction of both changes at the same time results in the *phthalocyanines* (**2** in Fig. 4, section 3). The absorption Q-bands characteristic of all these four types of compounds are shifted to the red with respect to porphyrins. Although the synthesis of porphyrins and phthalocyanines has been a matter of continuing scientific interest, the preparation of new congeners remains an expanding topic. On this regard, much less synthetic effort has been devoted to preparing contracted systems that contain only three pyrrole or isoindole units, respectively, instead of four, like *subporphyrins* (section 8),[7] *subporphyrazines* (section 5),[8] and *subphthalocyanines* (section 5).[9] The absorption Q-bands responsible for the colour of these compounds are shifted to the blue when compared to their higher homologues. Other contracted porphyrins, like corroles[10] as well as core-modified porphyrin analogues[11] have also been described. On the other hand, expanded porphyrins and phthalocyanines[12] differ from their basic relatives in their larger central core, while the extended conjugation features are retained. Among the limitless number of expanded systems that can be conceived, *sapphyrins*, *texaphyrins* and *superphthalocyanines* (section 7) are worthy of mention.

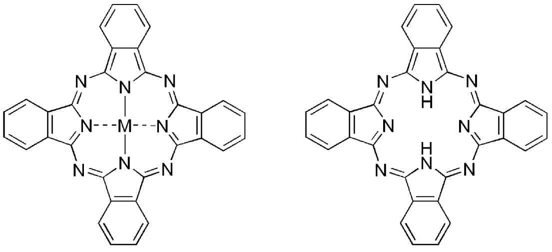


Fig. 4 The basic skeleton of a phthalocyanine (**2**) as a metal complex and as a free-base.

Over the last two decades we have been devoted to the synthesis of a large number of phthalocyanine derivatives for their application in different fields, as well as the in depth study of other classes of azaporphyrins and the development of new categories of azaporphyrin analogues. Herein we would like to highlight not only the colour properties and the applications of phthalocyanines, but also the possibility of preparing novel related porphyrinoids with different colour properties and, consequently, new emerging applications. All this work has given rise to a collection of azaporphyrin-based absorbers that covers the whole visible spectrum. In this article we review most of them, with the emphasis on their optical features and distinctive absorption regions.

3. From the violet to the red absorbers: the phthalocyanines

Among the plethora of natural and synthetic dyes and pigments, a particular macrocycle emerges with its own brilliant blue–green colour: the phthalocyanines. Phthalocyanines (Pcs, **2**, in Fig. 4)[13] are some of the best known synthetic porphyrin analogues, consisting of four isoindole units linked together through nitrogen atoms. They possess an 18 π-electron aromatic cloud delocalized over an arrangement of alternating carbon and nitrogen atoms. Therefore, Pcs can be referred to as tetrabenzotetraazaporphyrins. Numerous properties arise from their electronic delocalization, which makes them valuable in different fields of science and technology.

The replacement of the *meso* carbons in porphyrin molecules by *aza* linkages significantly breaks the accidental degeneracy of the $1a_{1u}$ and $1a_{2u}$ HOMO orbitals of the resulting azaporphyrins. Although not all the studies have been carried out on regular porphyrins, but also on the corresponding tetrabenzo-fused analogues, detailed analysis of all theoretical and experimental data has allowed to derive a general trend. Therefore, the sequential azasubstitution, that is, mono-, di-, tri- and tetrasubstitution, causes a progressive blue shift of the B-band and a red shift of the Q-band, with a concomitant decrease and increase, respectively, of the apparent absorption coefficients.[14–16] However, there is no systematic change in the bandwidth of the Soret band and the splitting of the Q-band for free-base derivatives.[17]

The situation is extreme for phthalocyanines, since these macrocycles also contain four fused benzene rings. The benzo groups break the accidental degeneracy of the top-filled molecular orbitals as well. Also in this case, we can follow Gouterman's model to explain the states that account for the first two or three allowed transitions in the UV–vis spectrum. The frontier orbitals of phthalocyanine complexes are still similar to those of the 16-atom and 18 π-electron polyene. However, new MOs located primarily on the peripheral portions of the π-system of the Pc ring have a major influence on the spectral properties. For phthalocyanine–metal complexes with D_{4h} symmetry, the $1a_{1u}$ and $1a_{2u}$ orbitals become widely separated, the $1a_{1u}$ lying well above the $1a_{2u}$, resulting in the observation of a red-shifted Q-band in the region of 670 nm, followed by a series of vibrational components, in addition to a hypsochromically shifted B-band, appearing around 300 nm (Fig. 5).

Furthermore, the mixing between the Q and B excited states is reduced. Consequently, the forbidden and very weak Q-band of the porphyrins acquires significant intensity in the case of Pc metal complexes and is observed as an intense absorption (Fig. 5).

Because of the influence of configuration interactions, only the $1a_{1u} \rightarrow 1e_g^*$ electronic transition that is responsible for the Q-band closely follows the predictions of the four orbital model (Fig. 6).[18] For closed-shell metals, the ground state has $^1A_{1g}$ symmetry, while the allowed π* states will be degenerate and have ^1E_u (x/y-polarized transitions) symmetry. Besides, the vibronic coupling in the excited state introduces z-polarized transitions with $^1A_{2u}$ symmetry. Spectral deconvolution and ZINDO calculations have indicated that there are in fact two transitions in the B region of the spectrum, corresponding to $1a_{2u} \rightarrow 1e_g^*$ and $1b_{2u} \rightarrow 1e_g^*$ one-electron transitions. Therefore, Gouterman's model has been modified to include separate B_1 and B_2 transitions that are

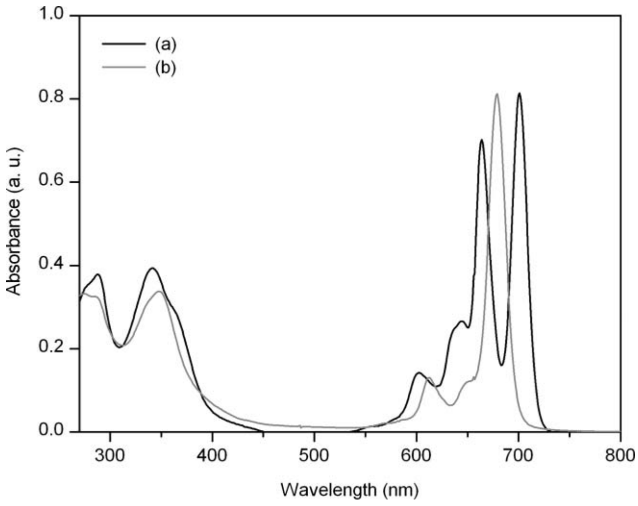


Fig. 5 Typical UV–vis spectra for a phthalocyanine as (a) a free-base and (b) a metal complex.

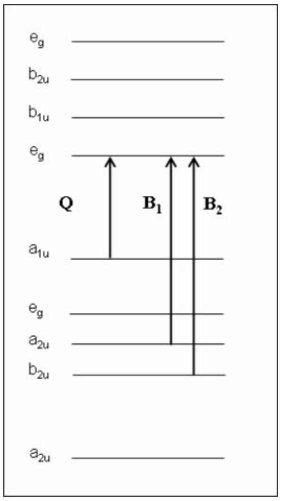


Fig. 6 The scheme of energy levels in metallated phthalocyanines with the first two $\pi \rightarrow \pi^*$ transitions, the Q- and B-bands, marked.

superimposed in the 300–350 nm region (Fig. 6).[18] In many cases, especially with cyanide as the axial ligand, these two bands are clearly resolved.

Parallel to that observed for porphyrins, the electronic spectrum of free-base phthalocyanines is characterized by a split Q-band, which occurs as a result of the reduction of symmetry from D_{4h} to D_{2h} on going from the metal complexes to the demetallated macrocycles (see Fig. 4 and 5). In this case all the states are non-degenerate, and so the major transitions are polarized in either x or y directions. z-Polarized transitions are also allowed by vibronic coupling in the excited states, but these states do not give rise to major intensity.[18c]

The above mentioned systems can host a variety of central metals in their inner cavity—more than 70 in the case of phthalocyanines—and support different types, either donor or acceptor, of peripheral and axial substituents. All these changes allow the tailoring of the electrophysical parameters over a broad range, giving rise to the modulation of their electronic properties and optical features. We will analyse the changes in the UV–vis spectra of phthalocyanines as a function of four different parameters:

1- The nature of the central metal.
2- The nature and position of the peripheral substituents.
3- The sequential addition of fused benzene rings.
4- The deviation from planarity.

3.1. The nature of the central metal

Unsubstituted phthalocyanine as a free base exhibits a split Q-band appearing at $\lambda_{max}(Q_x) = 698$ and $\lambda_{max}(Q_y) = 664$ nm.[19] Spectra of the anion measured in DMSO and stabilized by NH_4^+ appear like those of a regular complex with D_{4h} symmetry, with a $\lambda_{max}(Q)$ at 669 nm.[20] While for some phthalocyanine–metal complexes the Q-band is reasonably constant in energy on going from one metal complex to another, some metals induce a considerable shift of the same band. Conversely, the Q-bands are relatively insensitive to a change in the axial ligand, unless charge transfer (CT) bands are introduced. With respect to other absorptions, the envelope below 450 nm comprises several overlapping bands, that do move considerably in the last two cases.

Table 1 illustrates the values found for the Q-band in some representative examples of phthalocyanine–metal complexes. For a more comprehensive compilation see for example reference18*c*. From Table 1 it is possible to infer that the phthalocyanine Q-band usually shifts within a range of *ca.* 100 nm (between 620 and 720 nm) as a function of the metal size, coordination and

Table 1 Values found for the Q-band for some representative examples of phthalocyanine–metal complexes

Complex	Solvent	$\lambda_{max}(Q)$/nm	Ref.
Li_2Pc	CH_2Cl_2	667	22
MgPc	THF	670	22,23,24
$(imid)_2MgPc$	CH_2Cl_2	672	23,25*a*
ClAl(III)Pc	THF	675	26
Ge(II)Pc	DMSO	655	27
Sn(II)Pc	DMSO	682	27
Pb(II)Pc	DMSO	702	27
Cl_2SiPc	Py	699	28
$(OH)_2SiPc$	THF	667	28
R_2SiPc	THF	668	28
P(V)Pc	Py	653	29
VOPc	CH_2Cl_2	690	30
(*N*-Me-imid)$_2$Mn(II)Pc	DMA	667	31,32
Mn(II)Pc	Py	666	33,34
Mn(II)Pc	DMA	674	31*a*
LPcMn(III)-O-Mn(III)PcL	DMA	616	31*a*,32
(OH)Mn(III)Pc	DMA	718	32
L_2Fe(II)Pc	Py	650–670	35
[(σ-alkyl)Fe(II)Pc]$^-$	α-Cl naphthalene	707	36
[(CN)$_2$Fe(III)Pc]$^-$	CH_2Cl_2	685	37
[(CN)$_2$Fe(II)Pc]	CH_2Cl_2	667	37
[Fe(III)Pc]$_2$O	Py	620	38,39
Co(I)Pc	Py	704	40
Co(II)Pc	DMSO	657	41
(CN$^-$)$_2$Co(III)Pc	DMSO	673	41
Ni(II)Pc	α-Cl naphthalene	670	22
Cu(II)Pc	α-Cl naphthalene	678	42
Zn(II)Pc	CH_2Cl_2	671	25*a*,*b*
(Py)$_2$Ru(II)Pc	CH_2Cl_2	622	43
(CO)DMFRuPc	CH_2Cl_2	638	43
Py$_2$Rh(II)Pc	DMF	661	44
(CO)PyOs(II)Pc	$CHCl_3$	632	45
$LnPc_2$	CH_2Cl_2	665	46
(acac)$_2$ThPc	PhCN	684	47

oxidation state. A remarkable exception is constituted by the deep red titanium and manganese phthalocyanines that have been reported with Q-band maxima at strongly shifted values of 808 nm, and 808, 828 and 893 nm, respectively.[21] Compared to the free-base phthalocyanine, the species with closed-shell metals *e.g.* lithium(I), magnesium(II), or zinc(II) show λ_{max} values around 670 nm. In contrast, the specimens with open-shell metal ions that interact strongly with the phthalocyanine ring, such as iron(II), cobalt(II) or ruthenium(II) have Q-bands shifted to the blue with absorption maxima at around 630 to 650 nm.

The UV–vis spectrum of Li_2Pc corresponds to the spectrum of the Pc dianion Pc^{2-}. The spectrum of Mg(II)Pc shows the presence of an unperturbed phthalocyanine π-system. Similar spectra are displayed by Al(III)Pcs. With respect to the group 14, the Q-bands for the M(II)Pc complexes red shift on going down from Ge to Pb, to reach values of up to 700 nm. The spectrum of a P(V)Pc phthalocyanine has been reported to be that of a regular phthalocyanine complex, while vanadyl phthalocyanine exhibits quite red-shifted Q-bands.

The optical properties of phthalocyanines metallated with Mn, Fe and Co allow us to distinguish the oxidation state of the central metal very well. In addition, higher energies for the Q-bands are symptomatic of oligomerization through oxo-bridges. For example, the spectroscopic data reported for monomeric Mn(II)Pc in different solvents show that the solvents coordinate to the metal ion and that the well-resolved Q-band is sensitive to the axial ligand. Thus, the μ-oxodimer is prevalent in the presence of oxygen, water and mild acids and is uniquely characterized by a Q-band near 616 nm in DMA. On the other hand, absorption in the 710–720 nm region has been suggested as a diagnostic for monomeric (OH)Mn(III)Pc. Iron phthalocyanines also exhibit complicated axial ligand chemistry with consequences in their UV–vis features which have been deeply studied.[18c] In the presence of strongly coordinating solvents or ligands, the Q-band is observed in the 650–670 nm range. Besides, the Q-band region has been shown to be very sensitive to metal oxidation. Hence, λ_{max}(Q) appears at 667 for Fe(II), while for Fe(III) it is bathochromically shifted to 685 nm. μ-Oxodimers such as $[Fe(III)Pc]_2O$ absorbers exhibit the major visible region maximum at 620 nm. Similarly to MnPc and FePc, the spectroscopic properties of CoPc are dominated by reactions taking place at the metal center. The absorption spectrum of Co(I)Pc is marked by a rather weak Q-band at 704 nm, which shifts to the red in Co(II)Pc, appearing well resolved at 658 nm. Besides, a typical Co(III)Pc spectrum gives a Q-band at 673 nm. Because of its potential utility as a catalyst, Ru(II)Pc, has been extensively studied. L_2Ru(II)Pc typically shows a poorly resolved Q-band at 640 nm, due to the presence of additional bands that lie under the π→π* singlet (Fig. 7). Conversely to what could be expected, oxidation to Ru(III) does not readily occur.[48]

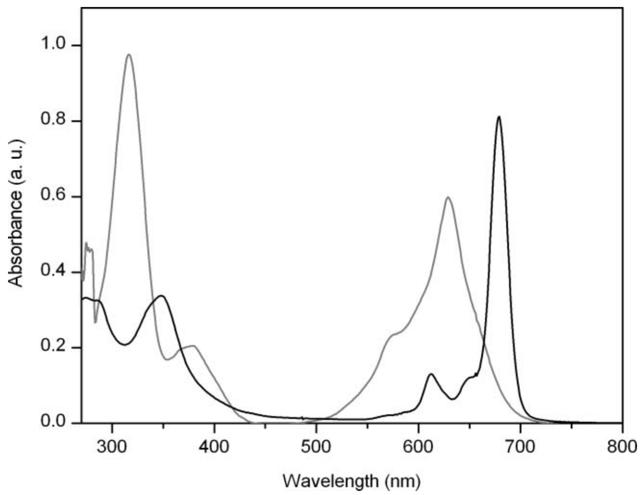


Fig. 7 UV–vis spectra of Zn(II)tetra-*tert*-butylphthalocyaninato (black line) and Ru(II)(pyridyl)$_2$(tetra-*tert*-butylphthalocyaninato) (grey line).

3.2. The nature and position of the peripheral substituents

Peripheral substituents play an important role in the tuning of the absorption bands of both phthalocyanine free base and the metal complexes. The Q-band can be shifted with the same additivity when the same kind of substituents are introduced at the same position of each benzene ring in a Pc macrocycle. The effect of introducing a plurality of substituents of different nature on each benzene unit has been recently examined.[49] Some representative examples are given in Table 2 and Fig. 8.[49–51]

Phthalocyanines **3** and **4** are constituted of a mixture of C_s, C_{2v}, D_{2h} and C_{4h} isomers, although for compounds **4** only the C_{4h} isomer is represented in Fig. 8. For the free base macrocycles $(Q_x + Q_y)/2$ indicates the Q-band's position. Hence, the reference values for the unsubstituted phthalocyanine free base (R = H, M = H_2) and zinc(II) complex (R = H, M = Zn) are found at $\lambda_{max}(Q) = 681$ and 670 nm, respectively. As can be deduced from Table 2, electron-donating groups shift the Q-band to longer wavelengths. The effect is stronger when the substituents are located at the α-positions of the benzene ring. Thus, for example Zn(II)phthalocyaninato

Table 2 Electronic absorptions found for the Q-bands of phthalocyanines bearing either electron donor or acceptor groups at the *ortho* or *meta* positions of the benzene rings

Phthalocyanine	M	Substituent	Number	Position	λ_{max}(Q)/nm
3a	Zn	NO_2	4	*m*	671
4a	Zn	NO_2	4	*o*	669
3b	Zn	SO_2Ph	4	*m*	677
4b	Zn	SO_2Ph	4	*o*	664
3c	Zn	OBu	4	*m*	674
4c	Zn	OBu	4	*o*	696
5c	Zn	OBu	8	*m*	674
6c	Zn	OBu	8	*o*	758
3d	Zn	SBu	4	*m*	687
4d	Zn	SBu	4	*o*	708
5d	Zn	SBu	8	*m*	707
6d	Zn	SBu	8	*o*	780
5e	Zn	CN	8	*m*	692
3f	Zn	*t*-Bu	4	*m*	675
7g	Zn	F	16	*o, m*	670
3h	Zn	COOH	4	*m*	685
5i	H_2	C_5H_{11}	8	*m*	689
3a	H_2	NO_2	4	*m*	693
4a	H_2	NO_2	4	*o*	676
3c	H_2	OBu	4	*m*	684
4c	H_2	OBu	4	*o*	706
5c	H_2	OBu	8	*m*	679
6c	H_2	OBu	8	*o*	753
3d	H_2	SBu	4	*m*	697
4d	H_2	SBu	4	*o*	721
5d	H_2	SBu	8	*m*	714
6d	H_2	SBu	8	*o*	804

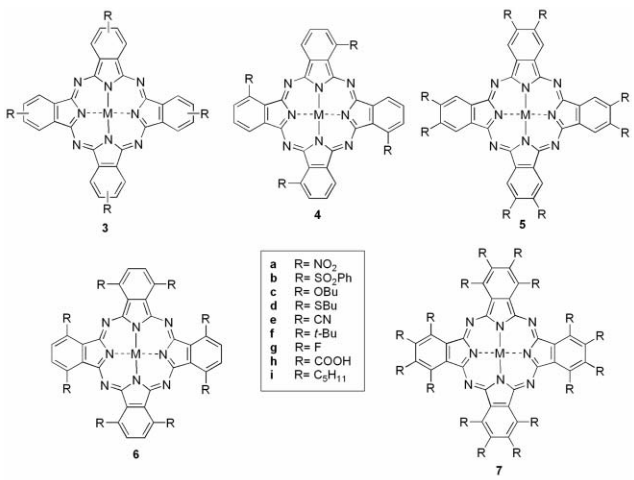


Fig. 8 Structures of the phthalocyanines that are the objects of comparison in Table 2.

4c, bearing four butoxy groups at the *ortho* positions exhibits a Q-band 22 nm bathochromically shifted with respect to its corresponding *meta*-substituted isomer **3c**. The effects are either similar or somewhat more pronounced for the corresponding free bases.

Octasubstitution produces additional red shift of the Q-bands, the results being markedly more evident for *ortho* substitution, which can shift the Q-band more than 100 nm towards lower energies (for example, 123 nm on going from Pc free base to **6d**). The influence of electron-donating groups on the phthalocyanine's electronic properties has been rationalized by carrying out molecular orbital calculations.[49] Thus, it has been postulated that substitution by electron-donating groups at the *meta* positions raises the energy of all frontier orbitals, this effect being slightly more pronounced for the HOMO than for the LUMO. Besides, substitution at *ortho* positions results in even larger destabilization of the HOMO and only slight destabilization of the LUMO. Since the Q-band can basically be described as a single transition from the HOMO to the LUMO frontier orbitals, these calculations correspond very well with experimental observations. The reason why the effect is stronger for *ortho* substitution can be found by taking into account the size of the carbon atomic orbital coefficients derived from the molecular orbital calculations. Specifically, the coefficients of the *ortho* carbon atoms are larger than those of the *meta* carbon atoms in the HOMO, so the extent of destabilization of this orbital by the introduction of electron-donating groups is larger when they are linked to the *ortho* positions, because this makes the HOMO–LUMO gap smaller.

With respect to electron-withdrawing groups, it has been calculated that there is a stabilization of the HOMO upon peripheral substitution with these kind of functions,[50] although in this case it is more difficult to establish a general behaviour. The tendency seems to be a variable red shift for *meta* substitution, while *ortho* substituents usually move the Q-band to shorter wavelengths (see Table 2).

3.3. The sequential addition of fused benzene rings

The sequential addition of fused benzene rings to the phthalocyanine structure implies an enlargement of the π-system and, as a consequence, the Q-bands shift to longer wavelengths and intensify, although the extent of the shift becomes smaller the larger the size of the macrocyclic ligand. With respect to the Soret bands, they also move to lower energy, but in this case they weaken and there is no regularity in the extent of the shift.[14a] The extent of the shift as a function of the π-system is represented in Fig. 9.

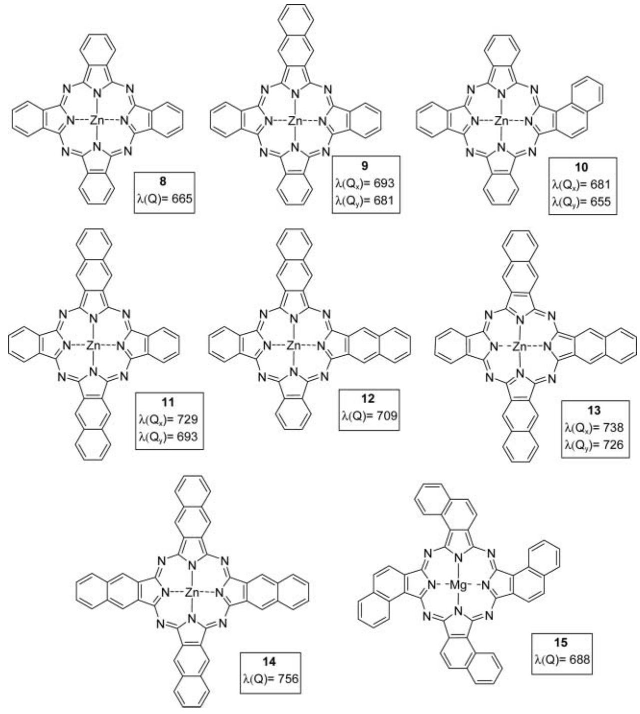


Fig. 9 Electronic absorptions found for the Q-bands of phthalocyanines upon the sequential addition of benzene rings.

The addition of one, two, three and four benzene rings results in bathochromic shifts of 22, 44, 67 and 91 nm, respectively, with respect to the phthalocyanine reference **8**.[52] Theoretical calculations have shown that on ring annulation, the separation between the $1a_{1u}$ and the $1a_{2u}$ levels increases, so the HOMO destabilizes significantly, while the LUMO remains almost constant. In addition, the reduction of symmetry on going from the D_{4h} system **8** to the D_{2h} and C_{2v} species breaks the degeneracy of the $1e_g$* orbitals to a degree which relates to the ratio of long to short axes in the molecule. The perturbation to the structure of Zn(II)Pc **8** results in different ring substitution patterns along the *x*- and *y*-axes for the D_{2h} isomer **11**, while the constitution is identical along the *x*- and *y*-axes in the case of the C_{2v} isomer **12**. In other words, the ratio of long to short axes for the isomer **12** is 1. Consequently, while the oppositely substituted species **11** usually display split Q-bands, for the adjacently substituted series **12**, a single Q-band, very similar in its shape to that exhibited by **8**, is observed. The extent of the splitting of the Q-band of the oppositely substituted species **11** has a parallel relationship with the lifting of the orbital degeneracy of the LUMO of these species. Thus, the larger the ratio, the larger the splitting. On the other hand, oblique ring fusion like that represented by compounds **10** and **15**[53] produces a relatively minor impact on the position of the Q-band.

3.4. The deviation from planarity

As a result of their smaller core size and fused benzene rings, metallophthalocyanines have extremely high planarity when compared to porphyrins.[54] For example, in contrast to the corresponding porphyrin, non-substituted Ni(II)Pc is perfectly planar.[55] However, larger metal ions such as Pb(II) and Sn(II) alter the Pc geometry to some extent.[56] Steric congestion of substituents causes distortion of the macrocycle as well. In this context, Cook and co-workers[57] have shown that the presence of alkyl chains close to the phthalocyanine core (*ortho* positions) provokes a deviation from planarity with concomitant modification of the Q-band position.

Further insight into the understanding of the relationship between the deformation of the phthalocyanine and its electronic properties was recently gained by Kobayashi and co-workers through a complete study of phthalocyanines bearing a different number of phenyl substituents at the *ortho* positions (Fig. 10).[58] In this series, the Q-band red shifts as the number of phenyl substituents increases. In the case of compound **16**, the bathochromic shift is very weak since in this macrocycle the two substituents do not provoke deformation. The influence of deformation on the electronic properties is evident when comparing **17** and **18**. Thus, although they both contain four phenyl substituents, the Q-band of **18** appears at a longer wavelength, by about 13 nm, since **17** is less distorted owing to the substitution at opposite rather than adjacent isoindole units. Stronger deformations induced by a larger number of substituents lead to stronger red shifting: 28 nm on going from **18** to **19** and 54 nm on going from **19** to **20**. The Q-band of the latter is located at 786 nm. Molecular orbital calculations show that the HOMO–LUMO gap is reduced as the number of phenyl substituents increases, but the destabilization of the HOMO orbital does not originate from the phenyl substitution but from the ring deformation.

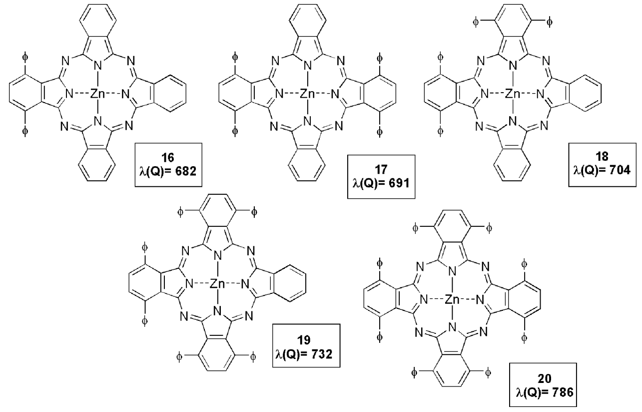


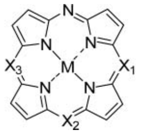
Fig. 10 Electronic absorptions found for the Q-bands of phthalocyanines upon sequential substitution with benzene rings.

Peripheral substitution combined with ring deformation affords phthalocyanines with a Q-band beyond 800 nm.[59] Thus, introduction of methoxy groups at the *para* position of the phenyl substituents in compound **20**, shifts the Q-band to 816 nm. In this case, further destabilization of the HOMO occurs due to increased electrostatic repulsion between the carbons at the *ortho* positions of the fused benzene rings and the electron-rich substituents. This compound, together with that reported in reference 21, is one of the few phthalocyanine derivatives that exhibits a Q-band above 800 nm.

4. Porphyrazines, the orange absorbers

As stated before, the replacement of the *meso* carbons in porphyrin molecules with *aza* linkages significantly breaks the accidental degeneracy of the $1a_{1u}$ and $1a_{2u}$ HOMO orbitals of the resulting azaporphyrins, with a concomitant influence on the UV–vis spectra of the resulting macrocycles.

Monoazaporphyrins **21** are porphyrin-like molecules with one nitrogen replacing one methine moiety at one of the *meso* positions (Fig. 11). Their synthesis was first reported by Fischer and Friedrich.[60] These derivatives can be prepared in good yields either from dipyrromethene[61] or from the corresponding porphyrin precursors.[62]



21 $X_1=X_2=X_3=C$ Mono-Azaporphyrin
22 $X_1=N$, $X_2=X_3=C$ or $X_2=N$, $X_1=X_3=C$ Di-azaporphyrin
23 $X_1=X_2=X_3=N$ Porphyrazine

Fig. 11 Structures resulting from the sequential replacement of the porphyrin *meso* carbons by *aza* bridges.

Available experimental data show a smooth red shift of the azaporphyrin Q-band with respect to the porphyrin, and a consequent increase in its intensity. Moreover, in the metal-free monoazaporphyrin, the Q-band splitting is larger than that corresponding to the metal free porphyrin, owing to the reduction of symmetry from D_{4h} to C_{2v} (see section 3.3). Thus, the free base 5-aza-mesoporphyrin absorption spectrum in chloroform exhibits a Q-band at $\lambda(Q_y) = 534$ nm ($\varepsilon = 1880\ M^{-1}\ cm^{-1}$) and $\lambda(Q_x) = 610$ nm ($\varepsilon = 2000\ M^{-1}\ cm^{-1}$).[63] Among the monoazaporphyrin derivatives, two classes of compounds exhibit a particularly marked bathochromically shifted Q-band. One of them is the *N*-methyl monoazaporphyrin,[64] where *N*-methylation is performed at the *meso* nitrogen ring, and the second class is constituted by azachlorin derivatives (Fig. 12), obtained by the reduction of one pyrrole ring. In this respect, Montforts and Gerlach have described a shift in the Q-band from 615 nm to 674 nm, for a monoazaporphyrin system and its azachlorin derivative respectively.[65]

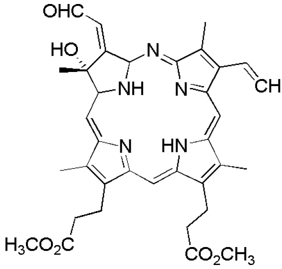


Fig. 12 Structure of azachlorin.

The second replacement of a methine bridge by nitrogen provides diazaporphyrin derivatives (**22**, Fig. 11). The introduction of two nitrogen atoms in the porphyrin structure produces an additional red shift of the Q-band with respect to the corresponding monoaza-congener. Hence, free base 5,15-diaza-mesoporphyrin exhibits in chloroform a Q-band at $\lambda(Q_y) = 545$ nm ($\varepsilon = 2960\ M^{-1}\ cm^{-1}$) and $\lambda(Q_x) = 620$ nm ($\varepsilon = 4950\ M^{-1}\ cm^{-1}$).[66] Moreover, most of the spectra displayed by the diazaporphyrin–metal complexes reported up until now exhibit the $\lambda(Q_x)$ band between 570 and 595 nm.

Porphyrazines (tetraazaporphyrins, Pzs) **23** (Fig. 11) constitute a class of macrocycles in which the four porphyrin *meso* carbons have been replaced by *aza* linkages.[6,15] These compounds can also be viewed as phthalocyanines lacking their fused benzene units. Contrasting with phthalocyanines, among the synthetic procedures available for the preparation of porphyrazines, the method reported by Linstead and co-workers still constitutes the most widely used.[6,67]

In porphyrazines, only the β-positions of the pyrrole moiety are available for chemical modification. However, despite this apparent limitation, tetraazaporphyrin structures offer the possibility of preparing a large number of derivatives with very different properties to those exhibited by phthalocyanines, including phthalocyanine-like macrocycles in which the benzene unit has been replaced by heterocyclic rings. The reason for most of the differences between Pzs and Pcs arises from the fact that in Pzs the peripheral functions are directly attached to the β-position of the pyrroles, so they can couple strongly to the macrocyclic core giving rise to systems with interesting physicochemical properties.

Similarly to phthalocyanines and other azaporphyrins, porphyrazine's electronic properties can be explained by modifying the Gouterman four orbital model and lifting the degeneracy of $1a_{1u}$ and $1a_{2u}$ HOMO orbitals. Thus, the Q-absorption arises from the almost pure HOMO→LUMO electronic transitions ($a_u \rightarrow b_{2g}$, b_{3g} for metal free macrocycles with D_{2h} symmetry or $a_{1u} \rightarrow e_g$ for metal complexes with D_{4h} symmetry).[68] As a result, on going from porphyrins to porphyrazines the Q-band shifts to longer wavelengths and intensifies. For example, the Q-band of free base porphyrazine in chlorobenzene is located at $\lambda(Q_y) = 545$ ($\varepsilon = 39800\ M^{-1}\ cm^{-1}$) and $\lambda(Q_x) = 617$ nm ($\varepsilon = 56200\ M^{-1}\ cm^{-1}$).[69] As for phthalocyanines, the electronic spectrum of a metallated *trans*-porphyrazine, with D_{2h} symmetry, generally shows a large splitting of the Q-band, as a consequence of its lower symmetry with respect to an identically substituted macrocycle (D_{4h}), while C_{2v} *cis*-porphyrazines show only a single Q-band.[70]

Commonly, porphyrazines possessing a heteroatom with a lone pair directly bound to the β-carbon atom of the pyrrole rings, like **24**, **26** and **27** (Fig. 13), constitute extended-conjugated systems and exhibit bathochromically shifted Q-bands, accompanied by relatively strong n→π* charge transfer bands in the window between the Soret and Q-bands.[71] The latter absorptions disappear when no π-donation is possible, for example upon peripheral metal complexation, as in compound **25** (Fig. 13). This peculiarity has been used for the design of multidentate porphyrazines with the ability of acting as metal ion probes.[72]

In the recent literature, ladder structures containing porphyrazine moieties have appeared. Thus, compound **28** (Fig. 13) constitutes a ladder dimer, which is rigidly constrained in a coplanar arrangement, and possesses an extended π-conjugated system.[73] Its electronic features are strongly influenced by the twelve peripheral auxochromic dimethylamino groups, as well as by its extended conjugation. Therefore, binuclear porphyrazine **28** exhibits a significantly red-shifted Q-band at 839 nm, that is, 134 nm red-shifted when compared with the corresponding octakis(dimethylamino) porphyrazine **24**.

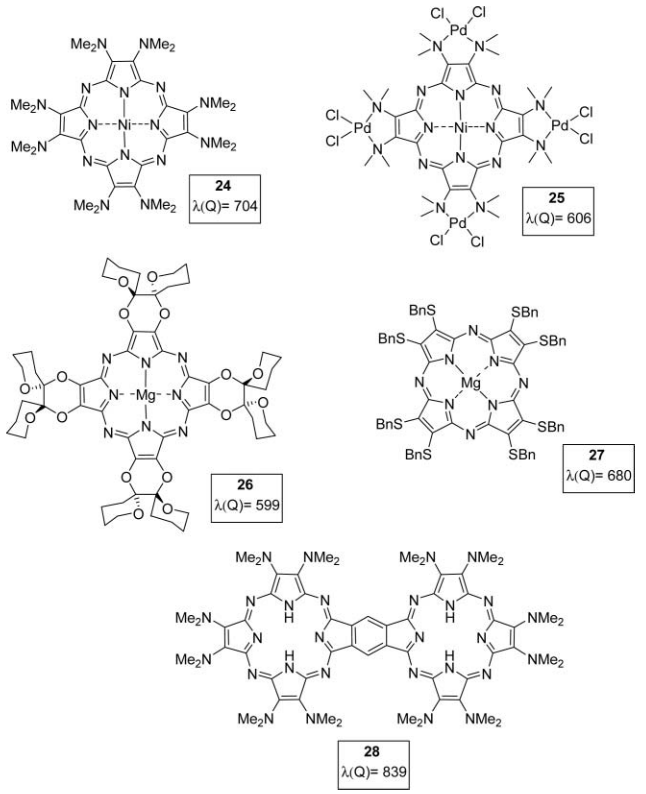


Fig. 13 Porphyrazines bearing heteroatoms directly attached to the pyrrole rings.

An alternative type of peripheral modification of the porphyrazine is β–β annulation. From the point of view of the number of π-electrons involved in the formation of the aromatic macrocyclic π-system, these porphyrazines can be considered as analogues of phthalocyanines. As for phthalocyanines, the sequential addition of fused benzene rings shifts the Q-band to longer wavelengths. In this respect, the possibility of fine-tuning the electronic properties of regular porphyrazines through successive ring-fusion has been studied.[74] Accordingly, Fig. 14 represents a porphyrazine series (**29–35**) in which the Q-bands shift slightly according to the nature (benzene, anthracene, naphthalene) and the number (mono-aromatic or di-aromatic) of the ring-fused peripheral substituents.

Furthermore, special attention has been dedicated to porphyrazine systems carrying externally annulated six-membered pyridine and pyrazine rings.[75,76] The Q-band position of these aza-analogues of phthalocyanines can be moved as a function of the number and position of the heterocyclic N-atom. For example, the Q-band of tetra-2,3-pyridinoporphyrazine (**36**, Fig. 15) appears blue-shifted by 20–50 nm with respect to the tetra-3,4-pyridinoporphyrazine (**37**, Fig. 15), the latter exhibiting a Q-band close to that observed for unsubstituted phthalocyanines.

More recently, Ercolani and co-workers have prepared and studied two novel families of porphyrazine macrocycles, namely the tetrakis(thia/selenodiazole)porphyrazines (**38**, Fig. 16), which are structurally similar to phthalocyanine.[75,77] The spectra of the S- and Se- complexes show intense absorptions in the Soret

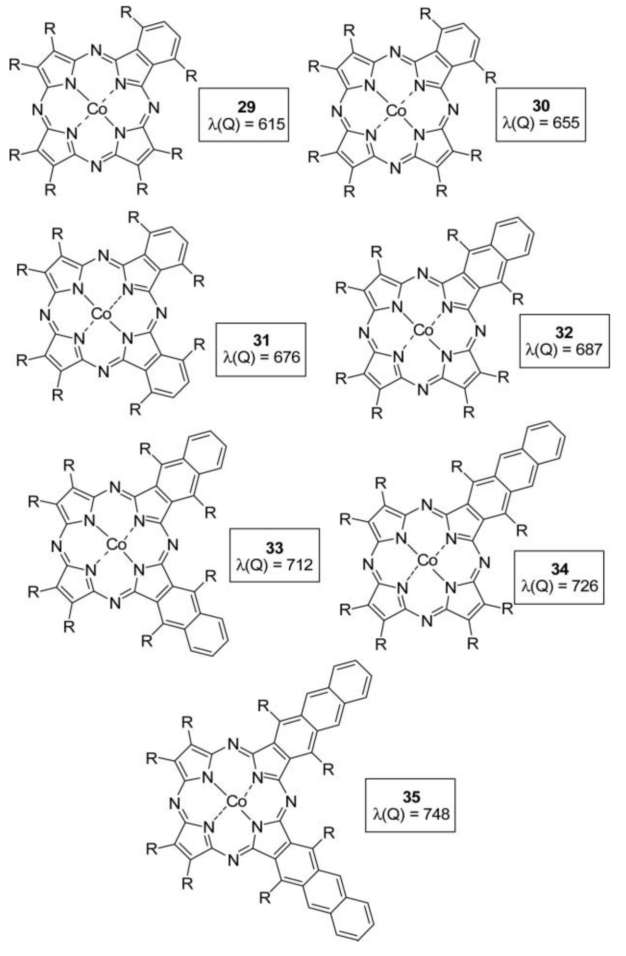
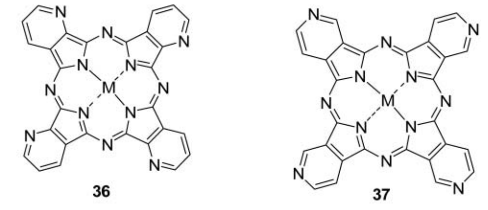


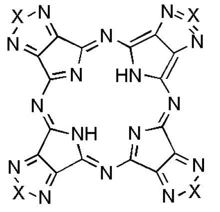
Fig. 14 The sequential addition of benzene rings to the porphyrazine molecule.



36 2,3-pyridinoporphyrazine

37 Tetra-3,4-pyridinoporphyrazine

Fig. 15 Tetrapyridinoporphyrazines **36** and **37**.



38 X= S, Se

Fig. 16 Tetrakis(thia/selenodiazole)porphyrazine.

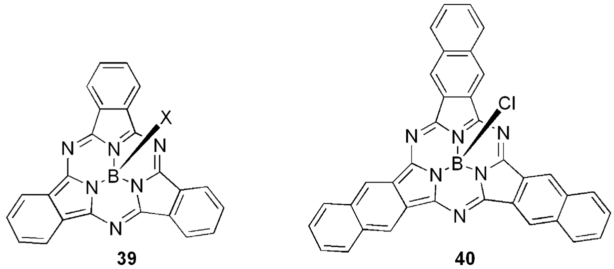
(300–400 nm) and Q-band (600–700 nm) regions, attributable to the allowed HOMO–LUMO intraligand $\pi \rightarrow \pi^*$ transitions.

When these four thia/selenodiazole rings are fused to the central porphyrazine core, the 22 π-electron chromophore is extended to a 32 π-electron chromophoric system. This extension causes a strong bathochromic shift with respect to the unsubstituted porphyrazine analogue, the selenium-containing species exhibiting the Q-band at longer wavelengths than the corresponding thiadiazole derivatives. In fact, the absorption spectra of the former compounds closely approaches the pattern observed for the phthalocyanine macrocycles, and constitutes a sign of an overall similar electronic distribution, as well as an extensive π-electron delocalization throughout the porphyrazine skeleton.

5. The green and yellow regions: SubPcs, SubPzs, TPcs and TPzs

5.1. Subphthalocyanines and subporphyrazines

Discovered in 1972 by Meller and Ossko[78] subphthalocyanines (SubPc, **39**) are the lowest homologues of phthalocyanines, as they consist of three isoindole units arranged around a central boron(III) ion (Fig. 17).[9] These cone-shaped macrocycles comprise an aromatic 14 π-electron structure. The reduction of the conjugated system from Pcs to SubPcs produces a drastic modification of the electronic properties, so that both Soret and Q-bands appear at shorter wavelengths (300 nm and 560 nm, respectively, see Fig. 20) with respect to the tetramers. Subphthalocyanines are synthesized in good yields by cyclotrimerization reactions of phthalonitrile precursors, in the presence of a boron derivative (typically a boron trihalide of BX_3 type). Synthetic modifications of SubPcs can be achieved at both the axial and the peripheral positions.

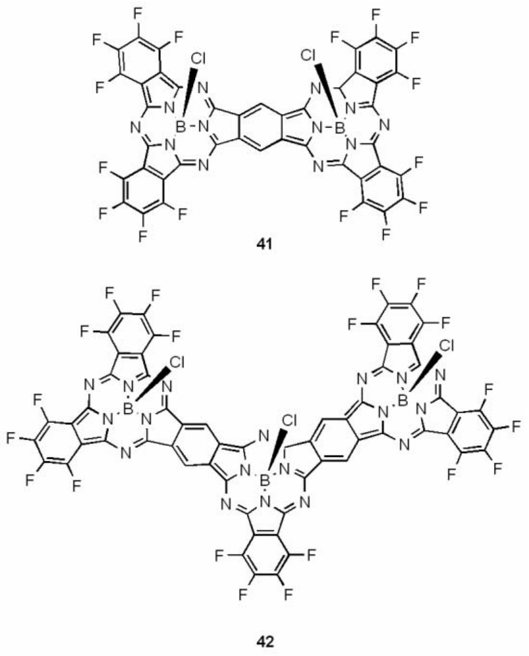


39

40

Fig. 17 Subphthalocyanine (**39**) and subnaphthalocyanine (**40**).

Molecular orbital calculations have been carried out to obtain a deeper understanding of the subphthalocyanine electronic absorption. Under C_{3v} symmetry, LUMO orbitals are doubly degenerate.[79] Besides, both HOMO and LUMO orbitals exhibit nodes at the boron atoms, this fact supporting the argument for the lack of electronic communication between the macrocycle and its axial substituents, and hence the small to negligible effect of these substituents on the electronic spectra of the subphthalocyanines.[80] In contrast, peripheral donor and acceptor functions do have an influence on the UV–vis features, tending to shift the Q-band of SubPcs towards longer wavelengths.[9] In particular, thioalkyl chains produce a strong red shift of 38 nm. Furthermore, by enlarging the π-system from that of a subphthalocyanine to that of a subnaphthalocyanine (Fig. 17, **40**), a 86 nm bathochromic effect (from 565 nm to 651 nm) occurs.[79,81] A larger extension to the π-conjugation of the SubPc aromatic core was achieved through the synthesis of fused dimers and trimers like **41** and **42** in Fig. 18.[82] The assembly of the subphthalocyanine dimer **41** moves the macrocycle's Q-band with respect to its monomeric analogue from 570 to 691 nm, this constituting a diagnostic for extension of the conjugation.



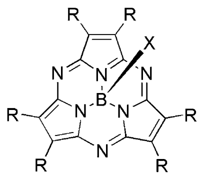
41

42

Fig. 18 Subphthalocyanine dimer (**41**) and trimer (**42**).

The new conjugated π-system involves the central benzene ring, as observed in electron density calculations. Of interest as well is the shape of the dimer's Q-band, four well-defined bands arising from the lower symmetry of **41**, compared to that of the monomer, which results in less orbital degeneration. This trend is also observed for the SubPc trimer **42**, the Q-band of which is located at 755 nm, that is, 180 nm red-shifted with respect to the corresponding monomer.

With respect to subporphyrazines (SubPzs, **43**, Fig. 19), they were recently unambiguously described.[8a] To the best of our knowledge only two examples of subporphyrazines had been reported at that time. However, the electronic properties described for these compounds do not match the data obtained in the paper above.[14,79,83] Subporphyrazines were prepared by treating disubstituted maleonitriles with boron trichloride. The easier axial substitution by nucleophiles in subporphyrazines, in comparison with subphthalocyanines, is thought to reflect the stronger interaction of the peripheral substituents with the macrocyclic core. Concerning the orange SubPzs, the formal removal of the three fused benzene rings from the subphthalocyanine skeleton causes a hypsochromic shift of the Q-band (Fig. 20), which appears at *ca.* 500 nm (as compared to the *ca.* 560 and 600 nm absorption bands seen in the cases of the corresponding pink subphthalocyanines and violet porphyrazines, respectively). Again, the stronger coupling of the peripheral substituents with the macrocycle is evidenced by dramatic changes in the electronic features that cannot be compared directly with the benzo-fused series. Thus, the efficient modulation of subporphyrazine's properties is possible, through peripheral substitution with selected specific functions, since the substituents are attached directly at the pyrrolic β-positions. As an example, peripheral functionalization with thioalkyl chains produces a 60 nm red shift (20 nm more than in the case of phthalocyanines) of the Q-band. But even more remarkable is the huge intensity of the charge transfer band appearing at 440 nm, which is responsible for the red colour displayed by these compounds (Fig. 20).



43

Fig. 19 Subporphyrazine (SubPz).

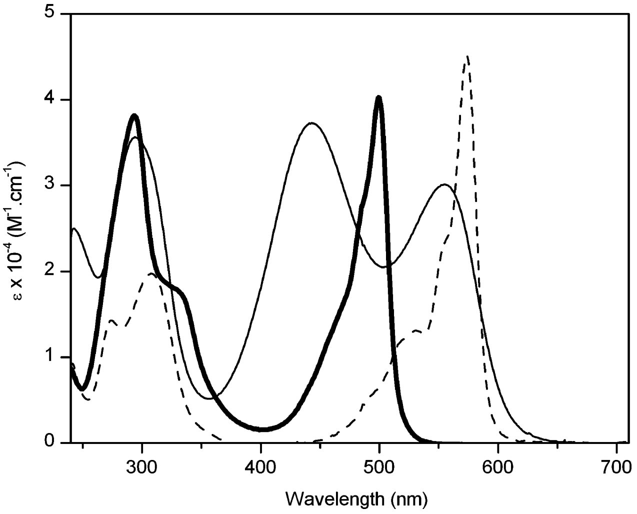
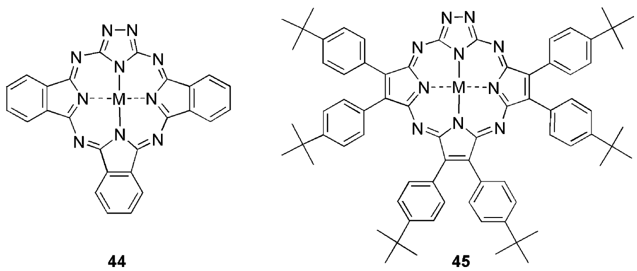


Fig. 20 UV–vis spectra of SubPc (dashed line) and SubPzs (R = propyl, thick line and R = thiopentyl, thin line).

5.2. Triazolephthalocyanines and triazoleporphyrazines

The search for non-centrosymmetrical phthalocyanines with different substituents at the periphery of the aromatic system, and with second-order non-linear optical properties,[84] led to the development of phthalocyanine-type macrocycles with an A_3B pattern in which A is an isoindole unit and B a heterocyclic moiety (benzene, pyridine, pyrrole, thiadiazole, triazole, *etc.*). Among the A_3B phthalocyanine analogues, those in which one isoindole subunit has been replaced by a 1,2,4-triazole have received the name of triazolephthalocyanines (TPc **44**, Fig. 21).[9d,85]

The introduction of this heterocycle into the phthalocyanine framework leads to a lower degree of electronic delocalization, which results in the hypsochromic shift of its Q-band in relation to the corresponding phthalocyanine absorption. Thus, for example, while the UV–vis spectrum of nickel(II) tetra-*tert*-butylphthalocyaninato is dominated by an intense absorption centred at 670 nm, tri-*tert*-butyl-substituted nickel(II) triazolephthalocyaninato displays its Q-band at the shorter wavelength of 623 nm.[85] In addition, a strong reduction of the symmetry on going from Pc to TPc accounts for a considerable splitting



44 **45**

Fig. 21 Triazolephthalocyanine (**44**) and triazoloporphyrazine (**45**).

of the optical absorptions (see Fig. 25). Modulation of the electronic properties of these aromatic macrocycles can be carried out by choosing appropriate peripheral functions,[85] by fusing additional benzene rings[86] or by preparing the corresponding triazoleporphyrazines (TPz **45** Fig. 21).[87] However, the most drastic modification of the UV–vis spectrum has been induced when the triazoleazaporphyrins are non-metallated, this difference being diagnostic of the non-aromatic character of the free base macrocycles.[87,88]

Thus for example, the UV–vis spectrum of the non-metallated compound **45** (Fig. 22), which does not match the characteristic porphyrazinic pattern, is constituted of four sharp absorptions at 323, 417, 486 and 530 nm. This means that the lowest energy band displayed by **45** as a free base is blue-shifted by 100 nm relative to the corresponding Ni(II) compound and by 136 nm when compared with the equivalent absorption of its parallel porphyrazine.[87]

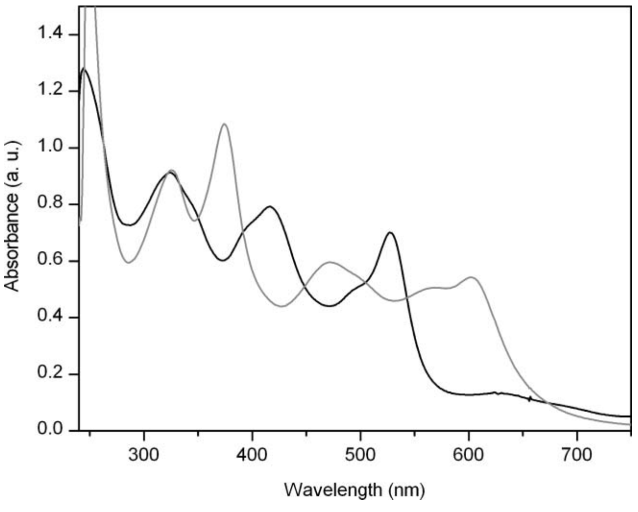
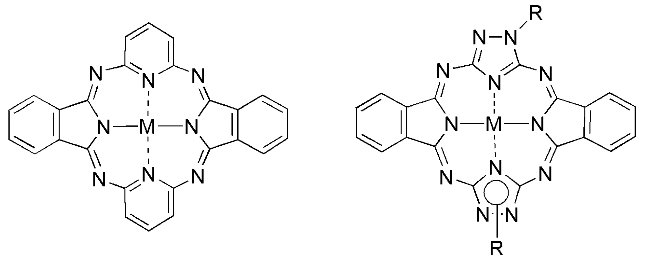


Fig. 22 Absorption spectra of triazoleporphyrazine **45** as a free-base (black line) and as the nickel(II) derivative (grey line).

6. Azaporphyrins absorbing in the violet–blue regions: the hemiporphyrazines

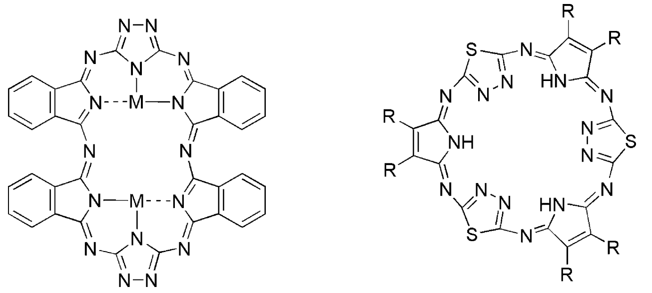
The absorption bands of the azaporphyrin derivatives can be further shifted to the blue, by replacing a second pyrrolic moiety in an A_3B system by another heterocyclic ring, to afford hemiporphyrazines (Fig. 23). Hence, these pigments may be defined as ABAB macrocycles that bear two oppositely facing pyrrole units and two other (hetero-)aromatic moieties.[9c,89,90] The first example of these non-aromatic, cross-conjugated compounds is the 28 π-electron macrocycle **46** (Hp, Fig. 23), which was reported by Elvidge and Linstead.[91] Compound **46**, together with that containing two triazole rings (THp, **47**) have received the greatest attention. A common feature of all hemiporphyrazines is their thermal stability and their lability in aqueous acidic media, owing to their Schiff base character. On the other hand, while phthalocyanines are aromatic systems of 18 π-electrons, hemiporphyrazines are 20 π-electron-systems that reveal a low-degree of electronic delocalization and a noticeable asymmetry of the ligand, facts that have decisive consequences on their electronic properties. Thus, their absorption spectrum (Fig. 25) has a non-porphyrazinic pattern, exhibiting all their absorptions in the ultraviolet–blue regions.



46 **47**

Fig. 23 Hemiporphyrazines.

As for the other types of macrocycle, the exact position of these bands can be fine-tuned by choosing appropriate metals and peripheral functionalization. But a more striking alteration can be achieved by modifying the macrocyclic structure itself. Thus, more recently, the first examples of expanded azaporphyrins **48** and **49** (Fig. 24) with hemiporphyrazinic character have been described.[92] Compounds **48** ([4+2] macrocycles) consist of 28 π-electron triazolehemiporphyrazine derivatives that coordinate two metal ions within their central cavity. The UV–vis spectra of these compounds show their bands bathochromically shifted with respect to the hemiporphyrazine tetramers, as a consequence of their extended conjugation. Hence, the lowest energy bands of compounds **48** appear at *ca.* 570 nm (up to 134–148 nm shifted towards longer wavelengths with respect to the corresponding hemiporphyrazine).



48 **49**

Fig. 24 Expanded triazolehemiporphyrazines.

Macrocycles **49** ([3+3] macrocycles) are 30 π-electron expanded heteroaza-porphyrinoids having a large cavity capable of accommodating three metal ions. Again, the absorption bands of these non-aromatic compounds are red-shifted when compared with regular hemiporphyrazines (Fig. 25), although to a lesser extent than the [4+2] macrocycles.

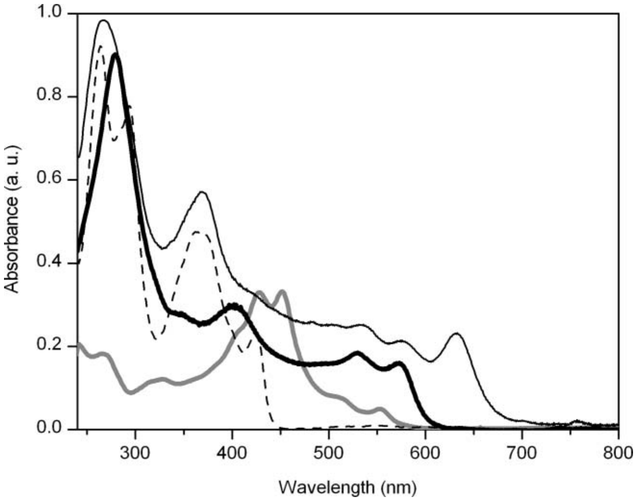


Fig. 25 UV–vis spectra of **48** (black thick line), **49** (grey thick line), **47** (dashed line) and TPc **44** (black thin line).

7. Beyond the red

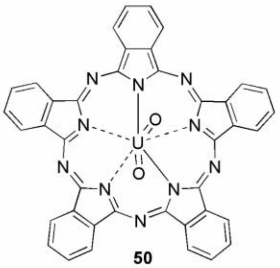
The absorption bands corresponding to phthalocyanine analogues containing extended π-systems appear at the other end of the visible spectrum. Two main strategies have been used to obtain these infrared absorbers:

1- Increasing the number of isoindole derivatives that the macrocycles are composed of, giving rise to the expanded superphthalocyanines and

2- Appending additional fused benzene rings at the naphthalocyanine periphery, affording the corresponding anthracyanines.

7.1. Superphthalocyanines

Constituted of five isoindole subunits, superphthalocyanines (Fig. 26, **50**) represent higher homologues of phthalocyanines. These pentapyrrolic macrocycles are obtained by UO_2^{2+} template condensation of phthalonitrile derivatives.[93] Uranyl superphthalocyanines are the only derivatives achieved until now, since on demetallation, immediate ring contraction to the corresponding four-membered macrocycle occurs.



50

Fig. 26 Superphthalocyanine.

The electronic spectra of the superphthalocyanines consist of an intense band at 910–940 nm (66 700 M^{-1} cm^{-1}) with a shoulder at 810 nm, which are analogous to the phthalocyanine Q-bands, but with a 200 nm red shift. The optical spectrum exhibited by **50** is understandable in terms of what it is known about the phthalocyanine UV–vis spectra: superphthalocyanine possesses a degenerate HOMO and a split LUMO, the latter arising from the severe buckling of the macrocycle. The observation of the two intense Q-bands can be explained by this lifting of the degeneracy of the LUMO with respect to the MPc, due to a lowering of the D_{5h} molecular symmetry, in a way comparable to the reduction of symmetry produced on going from the MPc to the Pc free base.[93b]

7.2. Anthracyanines

The structure of these extended conjugated macrocycles is represented by **51** in Fig. 27. Tetra-*tert*-butyl-anthracyanine's Q-band lies at 858 nm.[94] This corresponds to a 75 nm red shift with respect to the corresponding naphthalocyanine derivative. Nevertheless, this change is less important than that observed on going from tetra-*tert*-butylphthalocyanine to naphthalocyanine (85 nm). In other words, the Q-band shifts to longer wavelengths with annulation of additional benzene rings, but to a lesser extent with increasing molecular size. Accordingly, molecular orbital energy level calculations predict that the HOMOs destabilize with increasing molecular size, but to a minor degree, while the LUMOs of the metal-free derivatives remain almost constant. Upon metallation (M = Co, VO, Cu), anthracyanine Q-bands are blue-shifted for reasons still unclear. Thus, for example, the Q-band of the cobalt complex of tetra-*tert*-butylanthracyanine lies at 831 nm.[94b] Besides, few examples of substituted anthracyanines have been reported. Octaphenylanthracyanine's Q_x-band lies at 901 nm.[95] But a still lower-lying energy band among the anthracyanine derivatives was obtained for α-octa(isopentoxy)anthracyanine, the Q_x- and Q_y-bands of which appear at 980 and 954 nm, respectively.[95,96]

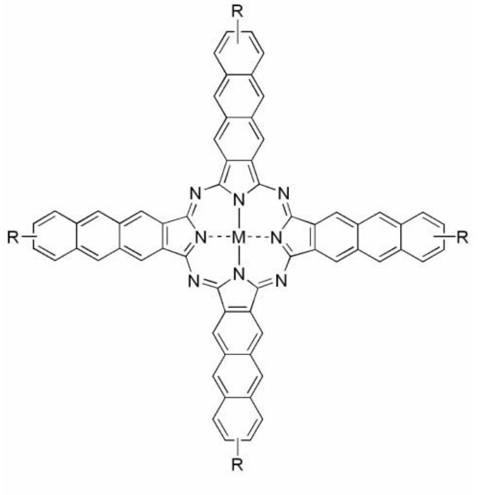


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Fig. 27 Anthracyanine.

8. Miscellaneous

The aim of this article is to offer a perspective on the preparation of tailor-made azaporphyrins and azaporphyrin analogues exhibiting their Q-band in a particular and predetermined region of the electromagnetic spectrum. However, three types of novel porphyrinic structures displaying absorptions at the two ends of the visible spectrum are very well worth a mention, especially because these structures with their optical features are virtually inaccessible for the azaporphyrin family. At the higher-energy end are the subporphyrins (Fig. 28). Described very recently, triarylsubporphyrins **52**[7] together with their subpyriporphyrin analogue **53**[97] represent the smallest known porphyrinic analogues and therefore, their absorption bands appear at the lowest known wavelength values among porphyrinic analogues, around 370 nm for the Soret band, and 450–500 nm for the weaker Q-like bands.

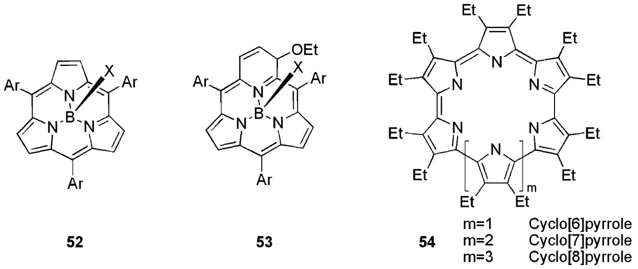

Fig. 28 Structures of subporphyrin (**52**) subpyridoporphyrin (**53**) and cyclo[m]pyrroles (**54**).

At the lower-energy end are the cyclo[m]pyrroles (m = 6,7,8) described by Sessler and co-workers (Fig. 28, **54**).[98] Such macrocycles contain no *meso* bridges but only 6,7 or 8 pyrrole units, respectively. Cyclo[m]pyrrole bis HCl salts are characterized by a very strong Q-band that dramatically red shifts on going from cyclo[6]pyrrole (792 nm) to cyclo[7]pyrrole (936 nm) to cyclo[8]pyrrole (1112 nm), thus reflecting the increased size of the respective framework involved (the $4n+2$ π-systems increase from 22 to 26 to 30 π-electrons). Indeed this cyclo[8]pyrrole turns out to be one of the expanded porphyrins with the longest wavelength Q-band. Only the doubly cationic hexathiarubyrin of Vogel and co-workers,[99] and the octaphyrin and nonaphyrin by Osuka and co-workers[100] display comparable low-energy band absorptions.

Finally, an extended-conjugated porphyrin sheet (Fig. 29, **55**) has been reported very recently, consisting of a combination of a central, strongly antiaromatic cyclooctatetraene, surrounded by four fused aromatic porphyrin rings.[101] The results of this unusual assemblage in terms of optical properties are three broad absorption bands, that of the lowest energy appearing at 1000–1500 nm, even though this band is considerably weaker than the other two.

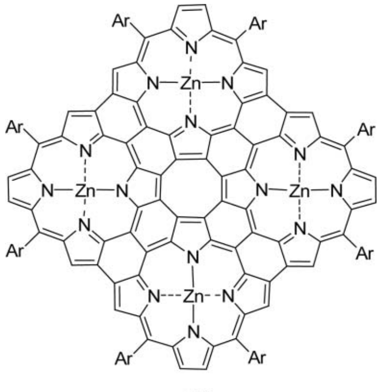

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Fig. 29 Porphyrin sheet.

9. Areas of technological interest based on the porphyrinoids' colour

The optical properties of phthalocyanines have found application in new areas of technological interest. In this section a brief non-exhaustive survey of a few relevant applications is given.

Organic solar cells based on phthalocyanines with extended absorption in the near IR region of the sunlight spectra are currently an important topic in the photovoltaic area. Phthalocyanines are perfectly suited for efficient photon harvesting and, therefore, for their integration in photovoltaic systems. They exhibit very high extinction coefficients, around 650–700 nm as mentioned before, where the maximum of the solar photon flux occurs. This is the reason why phthalocyanines have been incorporated as photosensitizers in both *low band gap molecular solar cells* and *dye sensitized solar cells* (DSSCs).[102]

Pcs are incorporated into low band gap molecular solar cells as antennas, usually in blends together with semiconducting polymers and/or acceptor counter-partners such as fullerenes.[103] In this context, a double-heterostructured copper phthalocyanine–fullerene thin-film has been described. Efficiencies exceeding 5.5% have been obtained by stacking two of these cells in series.[104] Doping-induced efficiency enhancement by doping rubrene into a copper phthalocyanine–C_{60} organic photovoltaic cell has been recently described, with an exceptionally high power conversion efficiency of 5.58%.[105] Tandem solar cells based on the combination of a poly(3-hexylthiophene-2,5-diyl)–PCBM and a copper phthalocyanine–fullerene subcell have been reported with power conversion efficiencies as high as 4.6%. The efficiency of the stacked devices is close to the sum of the efficiencies of the individual subcells.[106]

In dye sensitized solar cells (DSSCs) photons can be collected using phthalocyanine molecules that are placed over a layer of a wide band gap semiconducting material like a mesoporous metal oxide such as TiO_2.[107] Appropriately axially substituted titanium[108] and ruthenium phthalocyanines[109] represent an attractive new route to the development of efficient, red absorbing sensitizer dyes for DSSCs. It has also been reported that the use of tri-*tert*-butyl substituted zinc phthalocyanines in TiO_2 dye sensitized solar cells[110] not only avoided the formation of molecular aggregates but also arranged the excited states to permit directionality of the charge transfer from the phthalocyanines to the semiconductor's surface, thus allowing very high efficiencies of *ca.* 3.5%[111] Finally, a zinc phthalocyanine has been combined in a co-sensitized DSSC with another dye with a complementary absorption spectrum, thus obtaining a high overall device efficiency of 7.74%, which could not be achieved separately by each of them.[111] The photoresponse of the "molecular cocktail" extends up to 700 nm with photon-to-current conversion efficiencies of 72%.

Despite their lower absorption wavelengths (570 nm) with respect to Pcs, subphthalocyanines,[9] have been recently reported as active components in low band gap molecular solar cells. Thus, it has been described that a double-heterostructure boron-subphthalocyanine (SubPc)–C_{60} thin-film solar cell has more than doubled the open-circuit voltage (Voc) compared to a conventional CuPc–C_{60} cell.[112] The lower oxidation potential of the SubPc is responsible for this. Moreover, subphthalocyanine films in combination with fullerene (C_{60}) have been studied in a planar bilayer donor/acceptor heterojunction which shows a power efficiency of 3%.[113]

It is also remarkable that intrinsically bipolar materials in which the donor and acceptor photoactive units are covalently linked, like Pc–C_{60} dyads[114,115] have been described and PV devices have been prepared with a few of them. The goal was in this case the minimization of the morphological problems related to bulk heterojunctions. Also with this goal, Pc-based conjugated and non-conjugated polymers have been reported.[116]

In summary, the shifting of the Q-band to the red in particularly designed phthalocyanines and naphthalocyanines, with appropriate values of the HOMO and LUMO levels, and the development of effective p-type and n-type phthalocyanine and subphthalocyanine based materials, are challenges to be pursued in the photovoltaic area relating to porphyrinoids.

On the other hand, the potential application of phthalocyanines in organic light emitting devices (OLEDs) has also been suggested.[117] Thus, a conductive polymer comprising a linear main chain and a multitude of carrier transport structures based on Pcs has been claimed for applications in light emitting devices.[118] More recently[119] a series of new light emitting subphthalocyanines were synthesized having colour points covering the red–orange region of the visible spectrum. They were found to be of potential use as narrow band emitters for red-light emitting diodes. In spite of the narrow emission, the photostability of these subphthalocyanines does not meet the requirements of OLEDs operating duration, but it is believed that the synthesis of new representatives of this family and different approaches to the devices' construction will allow much higher future efficiencies.

Phthalocyanine derivatives and analogues with absorptions shifted to the blue, such as subphthalocyanines (570 nm), are required as active components in optical recording media like CDs, DVDs and even Blu-ray discs. Subporphyrazines, subporphyrins and even hemiporphyrazines could be targets for this goal. Most of the information in this regard is published in the form of patents.[120] Recently, an optical information recording medium has been described with two different read/write wavelengths based on phthalocyanine related systems. The invention consists in selecting a particular dye as a photoabsorptive material.[121]

On the other hand, phthalocyanines and related systems have also found applications in non-linear optics[84,122] in both second and third harmonic generation.[123,124] However, since comprehensive reviews and papers have been published this issue will not be treated in the current paper. Recent advances have also been made in the particular fields of optical limiting and two-photon absorption.[125]

Photodynamic therapy (PDT) is an emerging protocol for the non-invasive treatment of cancer or tumour-related diseases.[126] It is based on the photoactivation of selectively localized organic photosensitizers in neoplastic tissues, that can be activated with certain wavelengths of light so as to generate free radicals and singlet oxygen ($^1O_2$) that are toxic to cells and tissues. Molecular delivery systems with a high affinity for the target tissues can be used for increasing the selectivity by binding the photosensitizers to them. Typically water soluble compounds are needed. The most widely used PDT drug Photofrin® is a water-soluble, red powder consisting of a mixture of metal-free porphyrins. The active constituent consists of covalent dimers or small oligomers of porphyrin units joined by ether and ester linkages. The first generation PDT drug Photofrin® was approved in the U. S. for the treatment of obstructing cancer of the oesophagus and early stage cancer of the bronchus.[127] Synthetic modifications of porphyrins have been made in order to prepare compounds with better PDT efficiency. *meso*-Tetraphenylporphines, chlorins, bacteriochlorins, and benzoporphyrins,[128] among others, have been employed for this goal. Texaphyrins show a strong absorbance at 732 nm so treatment can be carried out effectively on a larger tumour or at a greater depth.[129]

Phthalocyanines represent promising second generation photodynamic agents since their Q-bands are more intense and red-shifted as compared with porphyrins. Pcs can produce long-lived triplet states with reasonable quantum yields and lifetimes, able to sensitize singlet oxygen formation.[130] They have been investigated for PDT applications for a long time.[131] The first described *in vivo* biomedical application of Pcs was the observation that uranium and copper complexes of a tetrasulfonated phthalocyanine were retained in experimental murine brain tumours.[132] Different metals were introduced to the central cavity of this particular Pc, aluminium and zinc being the most studied ones. A silicon phthalocyanine has been approved as a sensitizer for photodynamic treatment of oesophageal and early lung cancer.[133] Phthalocyanines currently represent a very active field of research for PDT applications.[134]

On the other hand, Pc analogues like naphthalocyanines have also been used in PDT. They exhibit a very strong absorption at higher wavelengths of *ca.* 800 nm, thus allowing the treatment of more profoundly localized neoplastic tissues[135] Subphthalocyanines (SubPcs) were shown to possess a very long-lived triplet state that is accessible with a nearly quantitative quantum yield,[9a,124] but their application for PDT is not so important since their Q-band is located at *ca.* 570 nm, too close to the tissues' absorption and below the so-called "therapeutic window". However, their lower homologues, the subnaphthalocyanines[136] possess the same photophysical characteristics as those of the SubPcs but with a Q-band shifted to the red at approximately 650 nm, making them potential candidates for PDT applications. The application of Pc-based PDT to other types of diseases like the treatment of restenosis after angioplasty and coronary artery disease (CAD)[137] would be a future expanding topic. In this respect the use of quantum dots and other nanoparticles linked to appropriate porphyrinoids[138] for making particular wavelengths accessible would be of great interest.

10. Conclusions

In conclusion, the accomplishments achieved so far in the porphyrinoid area related to the absorption wavelengths of its different members have been really remarkable in the last few years, but much more remains to be done. New synthetic developments, in conjunction with supporting theoretical studies, will provide a deeper understanding of the electronic nature of these porphyrinoids, thus allowing the design of new ones with improved performances and new applications in "colourful" technological areas.

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References

1 (*a*) P. Bamfield, *Chromic Phenomena: Technological Applications of Colour Chemistry*, Royal Society of Chemistry, Cambridge, 2001; (*b*) H. Zollinger, *Color Chemistry: Syntheses, Properties and Applications of Organic Dyes and Pigments*, John Wiley & Sons, New York, 3rd edn, 2003.

2 (*a*) *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, 2000, vol. 1–14; (*b*) *The Porphyrins*, ed. D. Dolphin, Academic Press, New York, 1st edn, 1978.

3 (*a*) M. Gouterman, *J. Mol. Spectrosc.*, 1961, **6**, 138–163; (*b*) M. Gouterman, in *The Porphyrins*, ed. D. Dolphin, Academic Press, New York, 2nd edn, 1978, vol. 3, part A, p. 1.

4 (*a*) A. M. Schaffer, M. Gouterman and E. R. Davidson, *Theor. Chim. Acta*, 1973, **30**, 9–30; (*b*) M. Gouterman, G. H. Wagniere and L. C. Snyder, *J. Mol. Spectrosc.*, 1963, **11**, 108–127; (*c*) C. Weiss, H. Kobayashi and M. Gouterman, *J. Mol. Spectrosc.*, 1965, **16**, 415–450; (*d*) A. J. McHugh, M. Gouterman and C. Weiss, *Theor. Chim. Acta*, 1972, **24**, 346–370; (*e*) A. M. Schaffer and M. Gouterman, *Theor. Chim. Acta*, 1972, **25**, 62–82.

5 M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc., London, Sect. A*, 1954, **67a**, 795–804.

6 M. S. Rodríguez-Morgade and P. A. Stuzhin, *J. Porphyrins Phthalocyanines*, 2004, **8**, 1129–1165.

7 (*a*) Y. Inokuma Yoon, Z. S. D. Kim and A. Osuka, *J. Am. Chem. Soc.*, 2007, **129**, 4747–4761; (*b*) Y. Takeuchi, A. Matsuda and N. Kobayashi, *J. Am. Chem. Soc.*, 2007, **129**, 8271–8281.

8 (*a*) M. S. Rodríguez-Morgade, S. Esperanza, T. Torres and J. Barberá, *Chem.–Eur. J.*, 2005, **11**, 354–360; (*b*) J. R. Stork, J. J. Brewer, T. Fukuda, J. P. Fitzgerald, G. T. Yee, A. Y. Nazarenko, N. Kobayashi and W. S. Durfee, *Inorg. Chem.*, 2006, **45**, 6148–6151.

9 (*a*) C. G. Claessens, D. González-Rodríguez and T. Torres, *Chem. Rev.*, 2002, **102**, 835–853; (*b*) T. Torres, *Angew. Chem., Int. Ed.*, 2006, **45**, 2834–2837; (*c*) N. Kobayashi, Synthesis and Spectroscopic Properties of Phthalocyanine Analogues, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego CA, 2003, vol. 15, pp. 161–262; (*d*) M. S. Rodríguez-Morgade, G. de la Torre and T. Torres, Design and Synthesis of Low-Symmetry Phthalocyanines and Phthalocyanine Analogues, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego CA, 2003, vol. 15, pp. 125–159.

10 (*a*) R. Paolesse, Syntheses of Corroles, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego CA, 2000, vol. 2, pp. 201–233; (*b*) C. Erben, S. Will, K. M. Kadish, Metallocorroles: Molecular Structure, Spectroscopy and Electronic States, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego CA, 2000, vol. 2, pp. 233–301.

11 L. Latos-Grazynski, Core-Modified Heteroanalogues of Porphyrins and Metalloporphyrins, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego CA, 2000, vol. 2, pp. 361–417.

12 (*a*) A. Jasat and D. Dolphin, *Chem. Rev.*, 1997, **97**, 2267–2340 and literature cited therein; (*b*) J. L. Sessler and S. J. Weghorn, in *Expanded, Contracted and Isomeric Porphyrins*, Pergamon, New York, 1st edn, 1997; (*c*) J. L. Sessler, A. Gebauer, S. J. Weghorn, Expanded Porphyrins, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego CA, vol. 2, 1999, pp. 55–124; (*d*) T. D. Lash, Syntheses of Novel Porphyrinoid Chromophores, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego CA and Burlington MA, 2000, vol. 2, pp. 125–200.

13 (*a*) *Phthalocyanines: Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, Weinheim, 1996, vol. 1–4; (*b*) *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego CA, 2003, vol. 15–20; (*c*) N. B. McKeown, *Phthalocyanine Materials: Synthesis, Structure and Function*, Cambridge University Press, Cambridge, 1st edn,1998; (*d*) G. de la Torre, M. Nicolau and T. Torres, in *Supramolecular Photosensitive and Electroactive Materials*, ed. H. Nalwa, Academic Press, New York, 1st edn, 2001, pp. 1–111; (*e*) G. de la Torre, C. G. Claessens and T. Torres, *Chem. Commun.*, 2007, 2000–2015.

14 (*a*) N. Kobayashi, H. Konami, Molecular Orbitals and Electronic Spectra of Phthalocyanine Analogues, in *Phthalocyanines: Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, Weinheim, Germany, 1st edn, 1996, vol. 4, pp. 343–403; (*b*) N. Kobayashi, Synthesis and Spectroscopic Properties of Phthalocyanine Analogues, in *Phthalocyanines: Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, Weinheim, Germany, 1st edn, 1993, vol. 2, pp. 97–161.

15 N. Kobayashi, meso-Azaporphyrins and their Analogues, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego CA, 2000, vol. 2, pp. 301–360.

16 J. Y. Hasegawa, T. Kimura and H. Nakatsuji, *J. Porphyrins Phthalocyanines*, 2005, **9**, 305–315.

17 (*a*) H. Ogata, T. Fukuda, K. Nakai, Y. Fujimura, S. Neya, P. A. Stuzhin and N. Kobayashi, *Eur. J. Org. Chem.*, 2004, 1621–1629; (*b*) J. Mack, N. Kobayashi, C. C. Leznoff and M. Stillman, *Inorg. Chem.*, 1997, **36**, 5624–5634.

18 (*a*) J. Mack and M. J. Stillman, *Coord. Chem. Rev.*, 2001, **219**, 993–1032; (*b*) J. Mack and M. J. Stillman, Electronic Structures of Metal Phthalocyanine and Porphyrin Complexes from Analysis of the UV–Visible Absorption and Magnetic Circular Dichroism Spectra and Molecular Orbital Calculations, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego, CA, 2003, vol. 16, pp. 43–116; (*c*) M. J. Stillman and T. Nyokong, Absorption and Magnetic Circular Dichroism Spectral Properties of Phthalocyanines Part 1: Complexes of the Dianion, Pc(-2), in *Phthalocyanines: Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, Weinheim, 1989, vol. 1, pp. 133–290; (*d*) J. Mack and M. J. Stillman, *Inorg. Chem.*, 2001, **40**, 812–814.

19 L. Edwards and M. Gouterman, *J. Mol. Spectrosc.*, 1970, **33**, 292–310.

20 D. L. Ledson and M. V. Twigg, *Inorg. Chim. Acta*, 1975, **13**, 43–46.

21 (*a*) C. C. Leznoff, L. S. Black, A. Hiebert, P. W. Causey, D. Christendat and A. B. P. Lever, *Inorg. Chim. Acta*, 2006, **359**, 2690–2699; (*b*) G. Mbambisa, P. Tau, E. Antunes and T. Nyokong, *Polyhedron*, 2007, **26**, 5355–5364.

22 M. J. Stillman and A. J. Thomson, *J. Chem. Soc., Faraday Trans. 2*, 1974, **70**, 805–814.

23 E. Ough, T. Tyokong, K. A. M. Creber and M. J. Stillman, *Inorg. Chem.*, 1988, **27**, 2724–2732.

24 T. Nyokong, Z. Gasyna and M. J. Stillman, *Inorg. Chem.*, 1987, **26**, 1087–1095.

25 (*a*) T. Nyokong, "*Spectroscopic and Electrochemical Studies of Phthalocyanines*", Ph.D awarded 1986 by the University of Western Ontario; (*b*) J. A. Duro and T. Torres, *Chem. Ber.*, 1993, **126**, 269–271.

26 Z. Ou, J. Shen and K. M. Kadish, *Inorg. Chem.*, 2006, **45**, 9569–9579.

27 P. Sayer, M. Gouterman and C. R. Connell, *Acc. Chem. Res.*, 1982, **15**, 73–79.

28 E. Ciliberto, K. A. Doris, W. J. Pietro, G. M. Reisner, D. E. Ellis, I. Fragala, F. H. Herbstein and M. A. Ratner, *J. Am. Chem. Soc.*, 1984, **106**, 7748–7761.

29 M. Gouterman, P. Sayer, E. Shankland and J. P. Smith, *Inorg. Chem.*, 1981, **20**, 87–92.

30 T. H. Huang and J. H. Sharp, *Chem. Phys.*, 1982, **65**, 205–216.

31 A. B. P. Lever, J. P. Wilshire and S. K. Quan, *J. Am. Chem. Soc.*, 1979, **107**, 3668–3669.

32 A. B. P. Lever, J. P. Wilshire and S. K. Quan, *Inorg. Chem.*, 1978, **20**, 761–768.

33 G. Engelsma, A. Yamamoto, E. Markham and M. Calvin, *J. Am. Chem. Soc.*, 1962, **66**, 2517–2531.

34 A. Yamamoto and L. K. Phillips, *Inorg. Chem.*, 1968, **7**, 847–852.

35 A. B. P. Lever, J. P. Wilshire, S. K. Quan, J. G. Jones and M. V. Twigg, *Inorg. Chim. Acta*, 1974, **10**, 103–108.

36 M. Tahiri, P. Doppelt, J. Fischer and R. Weiss, *Inorg. Chem.*, 1988, **27**, 2897–2899.

37 W. Kalz, H. Homborg, H. Kuppers, B. J. Kennedy and K. S. Murray, *Z. Naturforsch., B: Anorg. Chem. Org. Chem.*, 1984, **39b**, 1478–1489.

38 L. A. Bottomley, C. Ercolani, J. N. Gorce, G. Pennesi and G. Rossi, *Inorg. Chem.*, 1986, **25**, 2338–2342.

39 C. Ercolani, M. Gardini, K. S. Murray, G. Pennesi and G. Rossi, *Inorg. Chem.*, 1986, **25**, 3972–3976.

40 P. Day, H. A. O. Hill and M. G. Price, *J. Chem. Soc. A*, 1968, 90–93.

41 M. J. Stillman and A. J. Thomson, *J. Chem. Soc., Faraday Trans. 2*, 1974, **70**, 790–804.

42 Y. Iyechika, K. Yakushi and H. Kuroda, *Chem. Phys.*, 1984, **87**, 101–107.

43 T. Nyokong, Z. Gasyna and M. J. Stillman, *Inorg. Chim. Acta*, 1986, **112**, 11–15.

44 X. Munz and M. Hanack, *Chem. Ber.*, 1988, **121**, 235–238.

45 S. Omiya, M. Tsutsui, E. F. Meyer, I. Bernal and D. L. Cullen, *Inorg. Chem.*, 1980, **19**, 134–142.

46 M. M'Sadak, J. Roncali and F. Garnier, *J. Chim. Phys. Phys.-Chim. Biol.*, 1986, **83**, 211–216.

47 R. Guilard, A. Dormond, M. Belkalem, J. E. Anderson, Y. H. Liu and K. M. Kadish, *Inorg. Chem.*, 1987, **26**, 1410–1414.

48 M. S. Rodríguez-Morgade, M. Planells, T. Torres, P. Ballester and E. Palomares, *J. Mater. Chem.*, 2008, **18**, 176–181.

49 N. Kobayashi, H. Ogata, N. Nonaka and E. A. Luk'yanets, *Chem.–Eur. J.*, 2003, **9**, 5123–5134.

50 H. Shinohara, O. Tsaryova, G. Schnurpfeil and D. Wöhrle, *J. Photochem. Photobiol., A*, 2006, **184**, 50–57.

51 R. Li, X. Zhang, P. Zhu, D. K. P. Ng, N. Kobayashi and J. Jiang, *Inorg. Chem.*, 2006, **45**, 2327–2334.

52 (*a*) N. Kobayashi, H. Miwa and V. N. Nemykin, *J. Am. Chem. Soc.*, 2002, **124**, 8007–8020; (*b*) N. Kobayashi, J. Mack, K. Ishii and M. J. Stillman, *Inorg. Chem.*, 2002, **41**, 5350–5363.

53 E. H. Gacho, H. Imai, R. Tsunashima, T. Naito, T. Inabe and N. Kobayashi, *Inorg. Chem.*, 2006, **45**, 4170–4176.

54 T. Vangberg and A. Ghosh, *J. Am. Chem. Soc.*, 1999, **121**, 12154–12160.

55 J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 1937, 219–230.

56 M. K. Engel, *Kawamura Rikagaku Kenkyusho Hokoku*, 1996, 11–54.

57 I. Chambrier, M. J. Cook and P. T. Wood, *Chem. Commun.*, 2000, 2133–2134.

58 T. Fukuda, S. Homma and N. Kobayashi, *Chem.–Eur. J.*, 2005, **11**, 5205–5216.

59 T. Fukuda, T. Ishiguro and N. Kobayashi, *Tetrahedron Lett.*, 2005, **46**, 2907–2909.

60 H. Fischer and W. Friedrich, *Justus Liebigs Ann. Chem.*, 1936, **523**, 154–164.

61 J. P. Singh, L. Y. Xie and D. Dolphin, *Tetrahedron Lett.*, 1995, **36**, 1567–1570.

62 (*a*) S. Saito, S. Sumita, K. Iwai and H. Sano, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 3539–3547; (*b*) S. Saito and H. A. Itano, *J. Chem. Soc., Perkin Trans. 1*, 1986, 1–7.

63 S. Neya, T. Kaku, N. Funasaki, Y. Shiro, T. Iizuka, K. Imai and H. Hori, *J. Biol. Chem.*, 1995, **270**, 13118–13123.

64 A. M. Abeysekera, R. Grigg, J. Trochagrimshaw and K. Henrick, *Tetrahedron*, 1980, **36**, 1857–1868.

65 F. P. Montforts and B. Gerlach, *Tetrahedron Lett.*, 1992, **33**, 1985–1988.

66 S. Neya, H. Hori, K. Imai, Y. Kawamura-Konishi, H. Suzuki, Y. Shiro, T. Iizuka and N. Funasaki, *J. Biochem.*, 1997, **121**, 654–660.

67 (*a*) R. P. Linstead and M. Whalley, *J. Chem. Soc.*, 1955, 3530–3536; (*b*) M. E. Baguley, H. France, R. P. Linstead and M. Whalley, *J. Chem. Soc.*, 1955, 3521–3525.

68 (*a*) E. Orti, M. C. Piqueras, R. Crespo and J. L. Bredas, *Chem. Mater.*, 1990, **2**, 110–116; (*b*) L. K. Lee, N. H. Sabelli and P. R. Lebreton, *J. Phys. Chem.*, 1982, **86**, 3926–3931.

69 R. P. Linstead and M. Whalley, *J. Chem. Soc.*, 1952, 4839–4846.

70 L. Guo, D. E. Ellis, B. M. Hoffman and Y. Ishikawa, *Inorg. Chem.*, 1996, **35**, 5304–5312.

71 (*a*) S. Hachiya, A. S. Cook, D. B. G. Williams, A. G. Montalban, A. G. M. Barrett and B. M. Hoffman, *Tetrahedron*, 2000, **56**, 6565–6569; (*b*) D. P. Goldberg, A. G. Montalban, A. J. P. White, D. J. Williams, A. G. M. Barrett and B. M. Hoffman, *Inorg. Chem.*, 1998, **37**, 2873–2879; (*c*) C. S. Velazquez, G. A. Fox, W. E. Broderick, K. A. Andersen, O. P. Anderson, A. G. M. Barrett and B. M. Hoffman, *J. Am. Chem. Soc.*, 1992, **114**, 7416–7424.

72 (*a*) S. L. J. Michel, A. G. M. Barrett and B. M. Hoffman, *Inorg. Chem.*, 2003, **42**, 814–820; (*b*) L. S. Beall, N. S. Mani, A. J. P. White, D. J. Williams, A. G. M. Barrett and B. M. Hoffman, *J. Org. Chem.*, 1998, **63**, 5806–5817; (*c*) L. A. Ehrlich, P. J. Skrdla, W. K. Jarrell, J. W. Sibert, N. R. Armstrong, S. S. Saavedra, A. G. M. Barrett and B. M. Hoffman, *Inorg. Chem.*, 2000, **39**, 3963–3969; (*d*) S. J. Lange, J. W. Sibert, A. G. M. Barrett and B. M. Hoffman, *Tetrahedron*, 2000, **56**, 7371–7377.

73 G. Montalban, W. Jarrell, E. Riguet, Q. J. McCubbin, M. E. Anderson, A. J. P. White, D. J. Williams, A. G. M. Barrett and B. M. Hoffman, *J. Org. Chem.*, 2000, **65**, 2472–2478.

74 (*a*) N. Kobayashi, T. Ashida, T. Osa and H. Konami, *Inorg. Chem.*, 1994, **33**, 1735–1740; (*b*) N. Kobayashi, T. Ashida, K. Hiroya and T. Osa, *Chem. Lett.*, 1992, 1567–1570; (*c*) N. Kobayashi and T. Fukuda, *J. Am. Chem. Soc.*, 2002, **124**, 8021–8034.

75 P. A. Stuzhin, C. Ercolani, Porphyrazines with Annulated Heterocycles, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith, R. Guilard, Academic Press, San Diego CA, 2003, vol. 15, pp. 263–364.

76 S. V. Kudrevich and J. E. van Lier, *Coord. Chem. Rev.*, 1996, **156**, 163–182.

77 (*a*) M. P. Donzello, R. Agostinetto, S. S. Ivanova, M. Fujimori, Y. Suzuki, H. Yoshikawa, J. Shen, K. Awaga, C. Ercolani, K. M. Kadish and P. A. Stuzhin, *Inorg. Chem.*, 2005, **44**, 8539–8551; (*b*) E. M. Bauer, D. Cardarilli, C. Ercolani, P. A. Stuzhin and U. Russo, *Inorg. Chem.*, 1999, **38**, 6114–6120; (*c*) P. A. Stuzhin, E. M. Bauer and C. Ercolani, *Inorg. Chem.*, 1998, **37**, 1533–1539.

78 A. Meller and A. Ossko, *Monatsh. Chem.*, 1972, **103**, 150–155.

79 (*a*) N. Kobayashi, T. Ishizaki, K. Ishii and H. Konami, *J. Am. Chem. Soc.*, 1999, **121**, 9096–9110; (*b*) N. Kobayashi, *J. Porphyrins Phthalocyanines*, 1999, **3**, 453–467.

80 (*a*) M. S. Rodríguez-Morgade, C. G. Claessens, A. Medina, E. Gutiérrez-Puebla, I. Alkorta, J. Elguero and T. Torres, *Chem.–Eur. J.*, 2008, **14**, 1342–1350; (*b*) A. K. Eckert, M. S. Rodríguez-Morgade and T. Torres, *Chem. Commun.*, 2007, 4104–4106.

81 C. D. Zyskowski and V. O. Kennedy, *J. Porphyrins Phthalocyanines*, 2000, **4**, 707–712.

82 (*a*) C. G. Claessens and T. Torres, *Angew. Chem., Int. Ed.*, 2002, **41**, 2561–2565; (*b*) T. Fukuda, J. R. Stork, R. J. Potucek, M. M. Olmstead, B. C. Noll, N. Kobayashi and W. S. Durfee, *Angew. Chem., Int. Ed.*, 2002, **41**, 2565–2568; (*c*) R. S. Iglesias, C. G. Claessens, T. Torres, M. A. Herranz, V. R. Ferro and J. M. García de la Vega, *J. Org. Chem.*, 2007, **72**, 2967–2977.

83 J. Rauschnabel and M. Hanack, *Tetrahedron Lett.*, 1995, **36**, 1629–1632.

84 G. de la Torre, T. Torres and F. Agullo-Lopez, *Adv. Mater.*, 1997, **9**, 265–269.

85 (*a*) M. Nicolau, B. Cabezon and T. Torres, *Coord. Chem. Rev.*, 1999, **192**, 231–243; (*b*) F. Fernandez-Lazaro, A. Sastre and T. Torres, *J. Chem. Soc., Chem. Commun.*, 1994, 1525–1526.

86 M. Nicolau, B. Cabezon and T. Torres, *J. Org. Chem.*, 2001, **66**, 89–93.

87 M. K. Islyaikin, M. S. Rodríguez-Morgade and T. Torres, *Eur. J. Org. Chem.*, 2002, 2460–2464.

88 M. Nicolau, S. Esperanza and T. Torres, *J. Org. Chem.*, 2002, **67**, 1392–1395.

89 J. B. Campbell, US Pat. 2 765 308, 1956.

90 (*a*) F. Fernández-Lázaro, T. Torres, B. Hauschel and M. Hanack, *Chem. Rev.*, 1998, **98**, 563–575; (*b*) F. Fernández-Lázaro, J. de Mendoza, O. Mó, S. Rodríguez-Morgade, T. Torres, M. Yáñez and J. Elguero, *J. Chem. Soc., Perkin Trans. 2*, 1989, 797–803; (*c*) F. Fernandez-Lazaro, S. Rodríguez-Morgade and T. Torres, *Synth. Met.*, 1994, **62**, 281–285.

91 J. A. Elvidge and R. P. Linstead, *J. Chem. Soc.*, 1952, 5008–5012.

92 (*a*) M. S. Rodríguez-Morgade, B. Cabezon, S. Esperanza and T. Torres, *Chem.–Eur. J.*, 2001, **7**, 2407–2413; (*b*) M. K. Islyaikin, E. A. Danilova, L. D. Yagodarova, M. S. Rodríguez-Morgade and T. Torres, *Org. Lett.*, 2001, **3**, 2153–2156.

93 (*a*) E. A. Cuellar and T. J. Marks, *Inorg. Chem.*, 1981, **20**, 3766–3770; (*b*) T. J. Marks and D. R. Stojakovic, *J. Am. Chem. Soc.*, 1978, **100**, 1695–1705; (*c*) V. W. Day, T. J. Marks and W. A. Wachter, *J. Am. Chem. Soc.*, 1975, **97**, 4519–4527.

94 (*a*) N. Kobayashi, S. Nakajima and T. Osa, *Inorg. Chim. Acta*, 1993, **210**, 131–133; (*b*) N. Kobayashi, S. Nakajima, H. Ogata and T. Fukuda, *Chem.–Eur. J.*, 2004, **10**, 6294–6312.

95 W. Freyer, S. Mueller and K. Teuchner, *J. Photochem. Photobiol., A*, 2004, **163**, 231–240.

96 P. V. Bedworth, J. W. Perry and S. R. Marder, *Chem. Commun.*, 1997, 1353–1354.

97 R. Mysliborski, L. Latos-Grazynski, L. Szterenberg and T. Lis, *Angew. Chem., Int. Ed.*, 2006, **45**, 3670–3674.

98 (*a*) D. Seidel, V. Lynch and J. L. Sessler, *Angew. Chem., Int. Ed.*, 2002, **41**, 1422–1425; (*b*) T. Kohler, D. Seidel, V. Lynch, F. O. Arp, Z. P. Ou, K. M. Kadish and J. L. Sessler, *J. Am. Chem. Soc.*, 2003, **125**, 6872–6873.

99 M. Broring, J. Jendrny, L. Zander, H. Schmickler, J. Lex, Y. D. Wu, M. Nendel, J. G. Chen, D. A. Plattner, K. N. Houk and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2515–2517.

100 J. Y. Shin, H. Furuta, K. Yoza, S. Igarashi and A. Osuka, *J. Am. Chem. Soc.*, 2001, **123**, 7190–7191.

101 Y. Nakamura, N. Aratani, H. Shinokubo, A. Takagi, T. Kawai, T. Matsumoto, Z. S. Yoon, D. Y. Kim, T. K. Ahn, D. Kim, A. Muranaka, N. Kobayashi and A. Osuka, *J. Am. Chem. Soc.*, 2006, **128**, 4119–4127.

102 (*a*) C. J. Brabec, N. S. Sariciftci and J. C. Hummelen, *Adv. Funct. Mater.*, 2001, **11**, 15–26; (*b*) H. Hoppe and N. S. Sariciftci, *J. Mater. Res.*, 2004, **19**, 1924–1945; (*c*) N. S. Sariciftci, *Mater. Today*, 2004, **7**, 36–40; (*d*) C. Winder and N. S. Sariciftci, *J. Mater. Chem.*, 2004, **14**, 1077–1086; (*e*) S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz and J. C. Hummelen, *Appl. Phys. Lett.*, 2001, **78**, 841–843.

103 (*a*) R. Koeppe, N. S. Sariciftci, P. A. Troshin and R. N. Lyubovskaya, *Appl. Phys. Lett.*, 2005, **87**, 244102; (*b*) J. Rostalski and D. Meissner, *Sol. Energy Mater. Sol. Cells*, 2000, **63**, 37–47; (*c*) D. Wohrle and D. Meissner, *Adv. Mater.*, 1991, **3**, 129–138; (*d*) C. W. Tang, *Appl. Phys. Lett.*, 1986, **48**, 183–185.

104 J. G. Xue, S. Uchida, B. P. Rand and S. R. Forrest, *Appl. Phys. Lett.*, 2004, **85**, 5757–5759.

105 S. L. Lai, M. Y. Chan, M. K. Fung, C. S. Lee and S. T. Lee, *Appl. Phys. Lett.*, 2007, **90**, 203510.1–203510.3.

106 A. G. F. Janssen, T. Riedl, S. Hamwi, H. H. Johannes and W. Kowalsky, *Appl. Phys. Lett.*, 2007, **91**, 073519.1–073519.3.

107 (*a*) J. J. He, G. Benko, F. Korodi, T. Polivka, R. Lomoth, B. Akermark, L. C. Sun, A. Hagfeldt and V. Sundstrom, *J. Am. Chem. Soc.*, 2002, **124**, 4922–4932; (*b*) M. K. Nazeeruddin, R. Humphry-Baker, M. Gratzel and B. A. Murrer, *Chem. Commun.*, 1998, 719–720.

108 E. Palomares, M. V. Martinez-Diaz, S. A. Haque, T. Torres and J. R. Durrant, *Chem. Commun.*, 2004, 2112–2113.

109 (*a*) A. Morandeira, I. Lopez-Duarte, M. V. Martinez-Diaz, B. O'Regan, C. Shuttle, N. A. Haji-Zainulabidin, T. Torres, E. Palomares and J. R. Durrant, *J. Am. Chem. Soc.*, 2007, **129**, 9250–9251; (*b*) B. C. O'Regan, A. Morandeira, I. López-Duarte, M. V. Martínez-Díaz, J. Amparo, E. Palomares, T. Torres and J. R. Durrant, *J. Am. Chem. Soc.*, 2008, **130**, 2906–2907.

110 P. Y. Reddy, L. Giribabu, C. Lyness, H. J. Snaith, C. Vijaykumar, M. Chandrasekharam, M. Lakshmikantam, J. H. Yum, K. Kalyanasundaram, M. Graetzel and M. K. Nazeeruddin, *Angew. Chem., Int. Ed.*, 2007, **46**, 373–376.

111 J.-J. Cid, J.-H. Yum, S.-R. Jang, M. K. Nazeeruddin, E. Martínez-Ferrero, E. Palomares, J. Ko, M. Grätzel and T. Torres, *Angew. Chem., Int. Ed.*, 2007, **46**, 8358–8362.

112 K. L. Mutolo, E. I. Mayo, B. P. Rand, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.*, 2006, **128**, 8108–8109.

113 H. H. P. Gommans, D. Cheyns, T. Aernouts, C. Girotto, J. Poortmans and P. Heremans, *Adv. Funct. Mater.*, 2007, **17**, 2653–2658.

114 (*a*) D. Gonzalez-Rodriguez, T. Torres, D. M. Guldi, J. Rivera, M. A. Herranz and L. Echegoyen, *J. Am. Chem. Soc.*, 2004, **126**, 6301–6313; (*b*) M. A. Loi, P. Denk, H. Hoppe, H. Neugebauer, C. Winder, D. Meissner, C. Brabec, N. S. Sariciftci, A. Gouloumis, P. Vazquez and T. Torres, *J. Mater. Chem.*, 2003, **13**, 700–704; (*c*) D. M. Guldi, A. Gouloumis, P. Vazquez and T. Torres, *Chem. Commun.*, 2002, 2056–2057; (*d*) D. M. Guldi, J. Ramey, M. V. Martinez-Diaz, A. de la Escosura, T. Torres, T. Da Ros and M. Prato, *Chem. Commun.*, 2002, 2774–2775; (*e*) A. Sastre, A. Gouloumis, P. Vazquez, T. Torres, V. Doan, B. J. Schwartz, F. Wudl, L. Echegoyen and J. Rivera, *Org. Lett.*, 1999, **1**, 1807–1810; (*f*) M. Isosomppi, N. V. Tkachenko, A. Efimov, H. Vahasalo, J. Jukola, P. Vainiotalo and H. Lemmetyinen, *Chem. Phys. Lett.*, 2006, **430**, 36–40; (*g*) J. L. Sessler, J. Jayawickramarajah, A. Gouloumis, T. Torres, D. M. Guldi, S. Maldonado and K. J. Stevenson, *Chem. Commun.*, 2005, 1892–1894; (*h*) M. E. El-Khouly, O. Ito, P. M. Smith and F. D'Souza, *J. Photochem. Photobiol., C*, 2004, **5**, 79–104; (*i*) A. Gouloumis, A. de la Escosura, P. Vazquez, T. Torres, A. Kahnt, D. M. Guldi, H. Neugebauer, C. Winder, M. Drees and N. S. Sariciftci, *Org. Lett.*, 2006, **8**, 5187–5190.

115 A. de la Escosura, M. V. Martinez-Diaz, D. M. Guldi and T. Torres, *J. Am. Chem. Soc.*, 2006, **128**, 4112–4118.

116 M. V. Martinez-Diaz, S. Esperanza, A. de la Escosura, M. Catellani, S. Yunus, S. Luzzati and T. Torres, *Tetrahedron Lett.*, 2003, **44**, 8475–8478.

117 D. Hohnholz, S. Steinbrecher and M. Hanack, *J. Mol. Struct.*, 2000, **521**, 231–237.

118 M. Uehara, Seiko Epson Coporation, PCT Int. Pat. Appl. WO2006/075 724 A1, July 20, 2006.

119 D. D. Diaz, H. J. Bolink, L. Cappelli, C. G. Claessens, E. Coronado and T. Torres, *Tetrahedron Lett.*, 2007, **48**, 4657–4660.

120 (*a*) Y. Usami, T. Kakuta, T. Ishida, Fuji Photo Film Co., Ltd., Japan, Eur. Pat. Appl. 2004, EP 1 434 207 A2; (*b*) A. Zafirov, S. Rakovski, J. Bakardjieva-Eneva, L. Prahov, L. Assenova, F. Marrandino, Vivastar Mastering & Materials A.-G., Switz., PCT Int. Appl. 2002, WO 2002 080 158 A1.

121 H. Shimizu, D. Morishita, Taiyo Yuden K.K., EP1 622 138, 2006.

122 (*a*) H. S. Nalwa and J. S. Shirk, in *Phthalocyanines: Properties and Applications*, ed. C. C. Leznoff and A. B. P. Lever, VCH, New York, 1st edn, 1996, p. 79; (*b*) G. de la Torre, P. Vaquez, F. Agullo-Lopez and T. Torres, *Chem. Rev.*, 2004, **104**, 3723–3750; (*c*) G. de la Torre, P. Vazquez, F. Agullo-Lopez and T. Torres, *J. Mater. Chem.*, 1998, **8**, 1671–1683; (*d*) S. Flom, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, Boston, 2003, vol. 19.

123 (*a*) C. G. Claessens, D. Gonzalez-Rodriguez, T. Torres, G. Martin, F. Agullo-Lopez, I. Ledoux, J. Zyss, V. R. Ferro and J. M. García de la Vega, *J. Phys. Chem. B*, 2005, **109**, 3800–3806; (*b*) S. H. Kang, Y. S. Kang, W. C. Zin, G. Olbrechts, K. Wostyn, K. Clays, A. Persoons and K. Kim, *Chem. Commun.*, 1999, 1661–1662; (*c*) G. Olbrechts, K. Wostyn, K. Clays, A. Persoons, S. H. Kang and K. Kim, *Chem. Phys. Lett.*, 1999, **308**, 173–175; (*d*) G. Rojo, A. Hierro, M. A. Diaz-Garcia, F. Agullo-Lopez, B. del Rey, A. Sastre and T. Torres, *App. Phys. Lett.*, 1997, **70**, 1802–1804; (*e*) A. Sastre, T. Torres, M. A. Diaz-Garcia, F. Agullo-Lopez, C. Dhenaut, S. Brasselet, I. Ledoux and J. Zyss, *J. Am. Chem. Soc.*, 1996, **118**, 2746–2747; (*f*) M. A. Diaz-Garcia, F. Agullo-Lopez, A. Sastre, T. Torres, W. E. Torruellas and G. I. Stegeman, *J. Phys. Chem.*, 1995, **99**, 14988–14991; (*g*) E. M. Maya, E. M. Garcia-Frutos, P. Vazquez, T. Torres, G. Martin, G. Rojo, F. Agullo-Lopez, R. H. Gonzalez-Jonte, V. R. Ferro, J. M. García de la Vega, I. Ledoux and J. Zyss, *J. Phys. Chem. A*, 2003, **107**, 2110–2117; (*h*) M. A. Diaz-Garcia, I. Ledoux, J. A. Duro, T. Torres, F. Agullo-Lopez and J. Zyss, *J. Phys. Chem.*, 1994, **98**, 8761–8764; (*i*) M. A. Diaz-Garcia, I. Ledoux, F. Fernandez-Lazaro, A. Sastre, T. Torres, F. Agullo-Lopez and J. Zyss, *J. Phys. Chem.*, 1994, **98**, 4495–4497.

124 B. del Rey, U. Keller, T. Torres, G. Rojo, F. Agullo-Lopez, S. Nonell, C. Marti, S. Brasselet, I. Ledoux and J. Zyss, *J. Am. Chem. Soc.*, 1998, **120**, 12808–12817.

125 (*a*) M. Fournier, C. Pepin, D. Houde, R. Ouellet and J. E. van Lier, *Photochem. Photobiol. Sci.*, 2004, **3**, 120–126; (*b*) M. Drobizhev, A. Rebane, H. Spahini, C. W. Spangler and H. Wolleb, PCT Int. Appl., WO 2007 014 849, 2007.

126 (*a*) I. Okura, *Photosensitization of Porphyrins and Phthalocyanines*, Gordon and Breach, Amsterdam, The Netherlands, 2000; (*b*) I. J. MacDonald and T. J. Dougherty, *J. Porphyrins Phthalocyanines*, 2001, **5**, 105–129.

127 T. J. Dougherty and J. G. Levy, Photodynamic therapy (PDT) and clinical applications, *Biomedical Photonics Handbook*, ed. T. Vo-Dinh, CRC Press, Boca Raton FL, 2003, pp. 38/1–38/16.

128 (*a*) W. M. Sharman, C. M. Allen and J. E. van Lier, *Drug Discovery Today*, 1999, **4**, 507–517; (*b*) G. Jori, in *Handbook of Organic Photochemistry and Photobiology*, ed. W. M. Horspool, CRC Press, Boca Raton, 1st edn, 2003, pp. 1461–1470.

129 A. Synytsya, V. Kral, P. Matejka, P. Pouckova, K. Volka and J. L. Sessler, *Photochem. Photobiol.*, 2004, **79**, 453–460.

130 (*a*) E. Ben-Hur and W.-S. Chan, in *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilard, Academic Press, San Diego CA, 2003, vol. 19, pp. 1–35; (*b*) N. Brasseur, in *Comprehensive Series in Photochemical & Photobiological Sciences: Photodynamic Therapy*, ed. T. Patrice, Royal Society of Chemistry, Cambridge, 1st edn, 2003, vol. 2, p. 105.

131 E. Ben-Hur and I. Rosenthal, *Int. J. Radiat. Biol.*, 1985, **47**, 145–147.

132 (*a*) N. Brasseur, H. Ali, R. Langlois and J. E. van Lier, *Photochem. Photobiol.*, 1987, **46**, 739–744; (*b*) J. D. Spikes, *Photochem. Photobiol.*, 1986, **43**, 691–699.

133 M. Hu, N. Brasseur, S. Z. Yildiz, J. E. van Lier and C. C. Leznoff, *J. Med. Chem.*, 1998, **41**, 1789–1802.

134 K. Sakamoto, T. Kato, E. Ohno-Okumura, M. Watanabe and M. J. Cook, *Dyes Pigm.*, 2005, **64**, 63–71.

135 M. Shopova, M. Peeva, N. Stoichkova, G. Jori, D. Wohrle and G. Petrov, *J. Porphyrins Phthalocyanines*, 2001, **5**, 798–802.

136 S. Nonell, N. Rubio, B. del Rey and T. Torres, *J. Chem. Soc., Perkin Trans. 2*, 2000, **6**, 1091–1094.

137 (*a*) M. Magaraggia, A. Visona, A. Furlan, A. Pagnan, G. Miotto, G. Tognon and G. Jori, *J. Photochem. Photobiol., B*, 2006, **82**, 53–58; (*b*) D. J. Kereiakes, A. M. Szyniszewski, D. Wahr, H. C. Herrmann, D. I. Simon, C. Rogers, P. Kramer, W. Shear, A. C. Yeung, K. A. Shunk, T. M. Chou, J. Popma, P. Fitzgerald, T. E. Carroll, D. Forer and D. C. Adelman, *Circulation*, 2003, **108**, 1310–1315.

138 (*a*) S. Dayal and C. Burda, *J. Am. Chem. Soc.*, 2007, **129**, 7977–7981; (*b*) S. Dayal, Y. B. Lou, A. C. S. Samia, J. C. Berlin, M. E. Kenney and C. Burda, *J. Am. Chem. Soc.*, 2006, **128**, 13974–13975; (*c*) E. Zenkevich, T. Blaudeck, M. Abdel-Mottaleb, F. Cichos, A. Shulga and C. von Borczyskowski, *Int. J. Photoenergy*, 2006, 1–7; (*d*) A. C. S. Samia, S. Dayal and C. Burda, *Photochem. Photobiol.*, 2006, **82**, 617–625; (*e*) L. X. Shi, B. Hernandez and M. Selke, *J. Am. Chem. Soc.*, 2006, **128**, 6278–6279.