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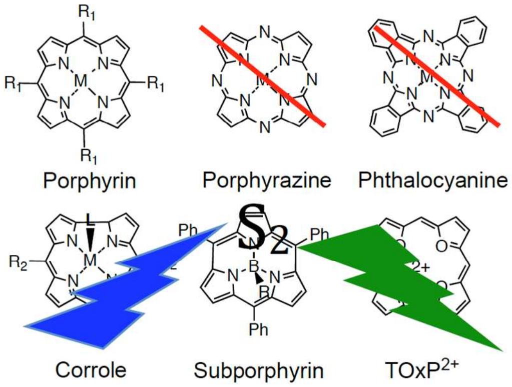

Text for Contents List:

Criteria for assigning observed blue-violet emission in porphyrinoids to anomalous $S_2 - S_0$ fluorescence are reviewed and suspicious assignments identified.

Concerning Correct and Incorrect Assignments of Soret ($S_2 – S_0$) Fluorescence in Porphyrinoids: A Short Critical Review

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Abstract:

The relaxation dynamics of electronically excited porphyrinoids are often measured by steady-state and time-resolved fluorescence methods. The unusual occurrence of measurable fluorescence from an upper excited singlet state (often identified as the second electronically excited singlet state, S_2) of some porphyrins has, in recent years, prompted a spate of mis-assignments of observed emission from other porphyrinoids excited in the near uv-violet regions of the spectrum. The criteria for correctly assigning fluorescence to a Soret excited state are reviewed. Questionable and mis-assigned reports are identified.

Introduction:

For many years the propensity of molecules to radiate with measurable intensity only from the lowest excited electronic state of a given multiplicity (Kasha's Rule[1]) guided the assignment of the observed emission spectra of electronically excited organic and organometallic compounds. Azulene was identified[1,2] as the first (and at the time, only) exception to this "rule"; its strongest fluorescence originates from its second excited singlet electronic state, S_2. However, as detector sensitivities improved and powerful laser excitation sources became generally available, additional exceptions were reported. Prominent among the genuine, anomalously emitting compounds are many non-alternant aromatic hydrocarbons (including azulene), aromatic acenes, polyenes, aromatic thiones, and a number of metalloporphyrins and metallated corroles. Several reviews identifying and characterizing these "anomalous" or "dual" emitters are now available[3-8].

Metalloporphyrins were among the first group of additional anomalous, dual emitters to be correctly identified.[9-13] A substantial number of them exhibit upper excited state fluorescence in the 400 – 450 nm region that can be excited directly by illumination in their strong Soret absorption bands in the near uv-violet region of the spectrum. In addition, some of these same anomalous emitters can produce delayed $S_2 \rightarrow S_0$ fluorescence (photon upconversion) indirectly via triplet-triplet annihilation following excitation in their lower energy Q bands[14-16]. In each case, their anomalous, blue-violet fluorescence is correctly identified as a relatively weak emission feature located immediately to the red of the Soret absorption band, with a small Stokes shift and quantum yield typically $\leq 10^{-3}$ in condensed media.

Because the anomalous fluorescence of metalloporphyrins and of several related compounds is now well-documented, it has become tempting to assign the blue-violet, apparently dual, emission that results from excitation in the Soret band spectral region of many porphyrinoids in a similar way. However, there are pitfalls associated with such a leap of faith. Stillman and coworkers[17] have noted that the blue-violet emission reported for several phthalocyanines, and often attributed to S_2 emission from their n,π* states, is likely best assigned to fluorescence from a photochemical impurity. The error in this emission assignment was identified primarily by TD-DFT calculations showing that n,π* states located between the Soret and Q states of phthalocyanines would have insufficient oscillator strength to produce emission with the measured intensity and lifetime. Similarly, the violet component of the dual (red + violet) fluorescence reported for several substituted porphyrazines used in biomedical imaging was reassigned to impurity emission by Motyka, *et al*.[18] based on (i) an incompatibility between the observed photophysics and that calculated for a porphyrazine Soret emitter, (ii) the fact that the violet emission excitation spectra did not coincide with the absorption spectra of the porphyrazines in the Soret region, and (iii) the observation that the violet emission grew in intensity with sample handling under visible illumination.

Criteria for assigning dual, anomalous fluorescence from Soret states

Despite the cautionary reports described above, there continue to be observations of blue-violet emission mis-assigned to to $S_2 - S_0$ fluorescence in a wide range of porphyrinoid systems. Reports requiring particular scrutiny include those in which the starting materials are contaminated, either during preparation or during sample examination. A wide variety of substituted metallated porphyrins prepared either as thin films or dissolved in glassy media and examined by steady state and time-resolved emission methods may be included in this group. Upper excited state fluorescence, either excited directly or produced indirectly by TTA, has indeed been observed from zinc tetraphenylporphyrin in polymethylmethacrylate (PMMA) thin films and other similar media.[16] However, these samples have typically been handled with extreme care to ensure that fluorescent impurities were not introduced in the preparation process or produced photochemically during examination.

Contrast this with, for example, the preparation of a wide variety of substituted metalloporphyrins dissolved in borate glasses.[19-24] Samples of the latter materials are prepared, typically, by (i) powdering mixtures of the metalloporphyrin with boric acid, (ii) heating the mixture in air to 150 °C for several hours to drive water from the boric acid and produce the viscous borate (B_2O_3) glass, (iii) briefly heating the glassy mixture to 230 °C to drive off bubbles and then (iv) pouring the mixture into a heated mould to obtain translucent discs for spectroscopic examination. This method subjects the samples to conditions in which chemical conversion of the metalloporphyrin to a variety of oxidized and ring-opened products is likely to occur even if the starting material is pure. The samples prepared this way do indeed produce substantial blue-violet fluorescence when excited at energies in the region of the Soret band of the uncontaminated metalloporphyrin. Indeed, readily visible blue fluorescence has been reported when some of these samples are excited at wavelengths further into the uv. However, the photophysical properties of the emitting species observed under these conditions[19-24] are not commensurate with an assignment of the emission to S_2 – S_0 fluorescence of the metalloporphyrin, even if it is dissolved in an alien solid state environment, as will be outlined in general terms below.

The photophysical properties of those porphyrinoids exhibiting true anomalous, dual emission have been identified.[13,25-31] In order for S_2 – S_0 anomalous emission to be readily observed by steady-state fluorometry, porphyrinoids must have structures that slow the rates of all parallel radiationless transitions competing with Soret excited state radiative decay. Using metalloporphyrins as examples, they should be rigid with planar (or near planar) macrocycles so that the S_2 and S_1 potential surfaces are "nested" to prevent strong interstate coupling. They should have relatively large S_2 – S_1 electronic energy gaps, be metallated with low atomic weight d^0 or d^{10} metal ions, and have no "dark" (*i.e.* charge transfer, d-d or n,π*) electronic states interleaved between the optically bright S_2 and S_1 states. The requirement of a relatively rigid structure implies that the Stokes shift between the Soret absorption and emission maxima will be small and that the S_2 – S_0 absorption and normalized corrected emission spectra will be good mirror images of one another. Figure 1 provides an example of these features for correctly assigned Soret-fluorescence of a metalloporphyrin.

Sets of metalloporphyrins with these properties often follow the energy gap law of radiationless transition theory.[26-30] That is, their excited state radiationless decay rates vary as the inverse exponent of the electronic energy difference between the S_2 (Soret or B band) and S_1 (Q band) coupled states – *i.e.*, in proportion to the inter-state Franck-Condon vibrational overlap factors, $\langle\chi_{S2}|\chi_{S1}\rangle^2$. In such cases $S_2 - S_1$ internal conversion is the only significant radiationless decay process of the Soret-excited state,[26-29] and the quantum yield of $S_2 - S_0$ fluorescence, ϕ_f, will be no greater than *ca.* 2×10^{-3}, for the following reasons. (i) The largest possible radiative decay constant, k_r, of the Soret excited state of a monomeric metalloporphyrin with an oscillator strength for the $S_2 - S_0$ transition near 1 will be $k_r \leq 5 \times 10^8$ s^{-1} (*i.e.* radiative lifetimes $\tau_r \geq 2$ ns, as calculated using a Strickler-Berg[32] treatment of the integrated molar absorptivity for the Soret absorption band). (ii) The $S_2 - S_1$ electronic energy gaps of the metalloporphyrins with the largest fluorescence quantum yields are at most *ca.* 7500 cm^{-1},[26-30] leading to a radiationless decay rate constant, k_{nr}, of the S_2 state no smaller than about 2.5×10^{11} s^{-1} when the energy gap law is followed (*i.e.* measured excited state lifetimes, $\tau_{S2} \leq 4 \times 10^{-12}$ s). (iii) When the energy gap law is not followed, for example as a result of strong interstate coupling or the interleaving of "dark" states between the optically bright π,π^* states,[33] the Soret states of porphyrinoids always exhibit still shorter lifetimes. (iv) Thus, using a standard steady-state kinetic analysis for parallel first order excited state decay processes, one obtains $k_r\tau_{S2} = \tau_{S2}/\tau_r = \phi_f \leq 2 \times 10^{-3}$ for the expected $S_2 - S_0$ fluorescence quantum yield. This is always more than an order of magnitude smaller than the quantum yield of fluorescence of the corresponding S_1 state for known anomalously fluorescing metalloporphyrins. Thus emission assigned to anomalous $S_2 - S_0$ fluorescence from a Soret state should be considered suspicious if: (i) the measured lifetime of the upper radiative state is longer than a few ps or (ii) the quantum yield of the anomalous emission is significantly larger than 10^{-3} or if its intensity is readily measurable with standard steady state instrumentation and is of a magnitude comparable to that of the S_1 fluorescence.

A steady-state fluorescence excitation analysis can also be used effectively to identify the absorbing state responsible for any observed fluorescence. When the excited state that is the terminus of an electronic absorption transition of a photochemically stable compound in a condensed medium is photostable and identical to the upper state that ultimately yields fluorescent emission, the corrected normalized fluorescence excitation spectrum should map closely onto the corresponding absorption spectrum, provided that the spectral bandwidths and solvent media are similar. For the anomalously emitting metalloporphyrins and related species, this is a strict test for identifying the state of origin of the fluorescence. In addition, a good mirror image relationship should exist between the Soret absorption band and the neighbouring red-shifted emission. A blue-violet fluorescence spectrum, corrected for reabsorption, that exhibits a large Stokes shift should be considered suspicious unless aggregated emitters are present. See Figures 2a and 2b for examples of comparisons of absorption and corrected excitation spectra for both correctly assigned and mis-assigned S_2 fluorescence emission in porphyrinoids.

Review of dual emission assignments in common porphyrinoids

The *caveats* and experimental “rules of thumb” described above can be used to identify both suspicious and robust assignments of observed emission originating in excited states of the absorber lying at higher energies than S_1, *i.e*. they may be used to identify truly anomalously emitting species. The following discussion uses the above criteria to identify both proven and suspicious assignments in various porphyrinoid classes.

In applying these criteria, one must be aware that a wide variety of variables can affect the measured lifetimes and radiative yields of any electronically excited species, including truly anomalously fluorescent porphyrinoids. In fluid solution and in glassy polymers, the effects of specific solute-solvent interactions such as hydrogen bonding or non-covalent solvent complexation can be significant, and most frequently result in reducing the both the S_2 fluorescence quantum yield and lifetime. These same measurables are also affected by solvent continuum properties such as polarizability and polarity. In the metalloporphyrins, for example, the $S_2 - S_1$ electronic energy gap decreases with increasing solvent refractive index, thereby increasing the rate of $S_2 - S_1$ internal conversion through increases in the corresponding Franck-Condon factors.[28] The effect of excitation wavelength should also be taken into account since intramolecular vibrational redistribution and intermolecular vibrational relaxation occur on times scales that typically either bracket or coincide with the S_2 lifetimes of the porphyrinoids. In this review, we apply the suggested criteria only to vibrationally thermalized excited states.

(i) *Metalloporphyrins*: All spectroscopically pure porphyrins metallated with low atomic weight diamagnetic d^0 or d^{10} metal ions appear to exhibit measurable anomalous fluorescence in inert media at room temperature unless they are substituted with groups designed to act as energy or electron acceptors. The largest $S_2 - S_0$ fluorescence quantum yields and the longest S_2 lifetimes appear to belong to the MTPP and MTBP species (M = Mg, Zn, AlX, GaX, SnX_2; X = Cl, OH; TPP =

tetraphenylporphyrin; TBP = tetrabenzoporphyrin).[25-34] Octaalkyl substitution of the macrocycle, metallation with heavier metals and/or metal ions too large to fit into the macrocycle cavity (e.g. Cd^{2+}) all result in substantially shorter lifetimes and proportionately smaller quantum yields of S_2 emission.[26-28,34] Anomalous emission from porphyrins metallated with several trivalent lanthanide ions has been reported,[11] but those with open shell structures have lower emission yields due to increased radiationless decay to charge transfer states. Pt(II) and Pd(II) porphyrins, used extensively as sensitizers, are essentially non-fluorescent from S_2 and have calculated lifetimes in the 10s of fs range.[35] Emission from the higher excited singlet states of porphyrins metallated with open shell metal ions such as Ni(II), Co(II), Cu(II), Mn(II), Cr(III), Fe(III) is either not observed or is extremely weak due to fast radiationless transitions from the initially-excited Soret state to nearby lower charge-transfer or d-d states.[33,34] For this reason the assignment of enhanced blue-violet emission from a Cu(II) porphyrin aggregated in a Langmuir-Blodgett film must be considered suspicious,[36] particularly in light of the recent report that the lifetime of the S_2 state of Cu(II)TPP in solution is only 63 fs.[37]

The free base porphyrins have much shorter Soret state lifetimes and smaller anomalous fluorescence quantum yields than their corresponding magnesium- or zinc-metallated counterparts for a similar reason.[38,39] The lower symmetry of the free base porphyrin results in lifting the degeneracy of the LUMO of the corresponding D_{4h} species for the planar metalloporphyrins. The Q (and to a lesser extent Soret) bands are split, effectively decreasing the electronic energy gap between the Soret state and the higher of the two Q band states. The smaller energy gap allows for a faster radiationless decay from Soret to Q (larger Franck-Condon factors for the transition), producing a shorter Soret state lifetime and a correspondingly smaller quantum yield of anomalous fluorescence. However, acidification of a free-base porphyrin to produce its dication (*e.g.* H_4TPP^{2+}) restores near-D_{4h} macrocycle symmetry and results in measurably stronger $S_2 – S_0$ emission.[34,39,40]

Anomalously fluorescent metalloporphyrins will retain their S_2 emission in a variety of media, including polymers[16] and ionic liquids,[41] provided samples are carefully prepared and are impurity free. Solvents do have a measurable effect, however, particularly those which hydrogen-bond to axial –OH groups in Sn(IV)-metallated or similar species[30,31] and those such as 4,4'-bipyridine which non-covalently bind in the axial position of species like ZnTPP and act as electron accepting quenchers of the S_2 state.[42] Simple substitution on pendant phenyl rings – for example by *p*-sulphonates[43,44] to render the porphyrin water soluble or by alkyl groups to make them more soluble in organic media – also has a relatively minor effect on the observed photophysics.

However, more extreme conditions of sample preparation, such as those described above for borate glasses,[19-24] clearly produce impurities derived from the metalloporphyrin. These impurities can absorb and emit in approximately the same spectral region as the Soret-bands of the intended solute, but the blue-violet emission from them is clearly mis-assigned to $S_2 – S_0$ fluorescence. The intensities are too large (relative to what is correctly assigned as Q band fluorescence), the emitting species often have lifetimes that are orders of magnitude too long and no excitation spectra are reported that identify the Soret state of the metalloporphyrin as the emitter.

(ii) ***Phthalocyanines and porphyrazines*****:** Anomalous upper state emission has been reported for a wide range of substituted phthalocyanines, porphyrazines and their analogues.[45-65] However, many of these reports[52, 56-64] are now known to be mis-assignments, likely due to impurities,[17,18] and others not yet experimentally re-investigated must be considered suspicious. Unfortunately, early mis-assignments seem to have been propagated most extensively in the literature for this group of porphyrinoids. TD-DFT calculations by Stillman and co-workers[17] have demonstrated that substitution of CH segments of a porphyrin macrocycle by N atoms having in-plane lone-pair electrons introduces sets of n,π* states in the phthalocyanine that are located between its optically bright π,π* states associated with the Q and B (Soret) band absorptions. Although "dark" (*i.e.* accessed by one-photon absorptions with low oscillator strengths[17]) these n,π* states nevertheless provide accessible additional paths for ultrafast radiationless decay of an initially populated Soret state, substantially shortening the lifetime of the initially populated upper state and proportionately reducing its radiative yield. The same structural features also mitigate against observing measurable $S_2 - S_0$ fluorescence from the porphyrazines[18] and other porphyrinoids containing non-pyrrole nitrogen atoms in their macrocycles. If weak Soret fluorescence is present in these near uv-excited molecules, it is clearly masked by much stronger impurity emission.

(iii) ***Metallated corroles*****:** Corroles are tetrapyrroles that possess one fewer bridging methine groups than the corresponding porphyrins. Such a variant of the porphyrin structure is expected to produce domed metallated stuctures with lower symmetry, but ones in which no additional dark states are interleaved between S_2 and S_1. Anomalous S_2 – S_0 fluorescence from two corroles metallated with Al and Ga has been reported (Scheme 1).[66,67] The S_2 lifetimes are short (<1 ps) and the radiative yields are small (*ca.* 10^{-4}) as required.

(iv) ***Subporphyrins***: One interesting recent report[68] of the upper excited state photophysics of subporphyrins (Scheme I) clearly correctly identifies anomalous S_2 – S_0 emission from the Soret excited state. These subporphyrins possess the general characteristics required of anomalously fluorescent molecules; they are diamagnetic, have neither macrocycle nitrogen nor heavy atoms and exhibit moderately large S_2 – S_1 electronic energy spacings. The measured upper state lifetimes are *ca*. 300 fs, about a factor of 5 or 6 faster than the corresponding ZnTPP standard in similar solvents. Their faster rates of S_2 – S_1 internal conversion compared with the planar D_{4h} macrocycles of the metalloporphyrins themselves have been attributed to their domed structures.[68]

(v) ***Other porphyrinoids***: Over 7000 papers are retrievable by Sci-Finder© using the search terms “fluorescence” and any of “porphyrin, porphazine, phthalocyanine, corrole, subporphyrin or porphyrinoid” or “dual, Soret or anomalous”. In this review, approximately 100 of these papers have been examined for the occurrence of blue-violet fluorescence mis-assigned to excited states, S_n (n > 1), higher in energy than the lowest energy electronically excited singlet state; 69 of these have been referenced. It is clear that a complete review of all 7000 papers would uncover still more suspicious assignments. Although it is impractical to for a single research group to re-measure all of the materials for which dual emission has been reported, readers of this review can apply the *caveats* and rules of thumb outlined above to determine for themselves if dual fluorescence assignments are valid.

The correlations and rules of thumb generated for the porphyrins might also prove applicable to closely related classes of compounds such as their oxo-analogs and the bridged annulenes. For example, the tetraoxoporphyrin dication, $TOxP^{2+}$ (Scheme I), which has been synthesized (as the perchlorate) by Vogel, *et al.*[69], exhibits dual (violet + yellow) fluorescence when excited in its Soret-equivalent absorption band at 370 nm.[40] The violet fluorescence is unusually intense but is correctly assigned to the $S_2 - S_0$ transition owing to its very large oscillator strength ($f = 1.1$) and the large $S_2 - S_1$ electronic energy spacing of over 9000 cm^{-1} which slows the rate of $S_2 - S_1$ internal conversion. Based on the previous energy gap law correlations developed for the magnesium and zinc metalloporphyrins and the azulenes,[28] such an electronic energy gap should result in an S_2 lifetime of about 25-30 ps. This compares with a measurement[68] of $\tau_{S2} < 100$ ps and a Strickler-Berg[32] calculation of $\tau_{S2} \sim 40$ ps. All of the other criteria for assigning the violet fluorescence to the $S_2 - S_0$ transition of $TOxP^{2+}$ also hold; the molecule is rigid and planar, the Stokes shift is small, the Soret absorption and violet emission spectra are good mirror images, it has no atoms with lone pairs that contribute interleaved n,π* excited states between S_2 and S_1, and it has no heavy atoms.

Conclusions:

The criteria and "rules of thumb" for correctly assigning blue-violet emission in porphyrinoids to anomalous $S_2 - S_0$ fluorescence have been reviewed. A large number of suspicious and some clearly incorrect assignments have been identified. The robustness of these criteria for assigning the blue-violet component of dual fluorescence in unusual porphyrinoids and porphyrin analogues is encouraging.

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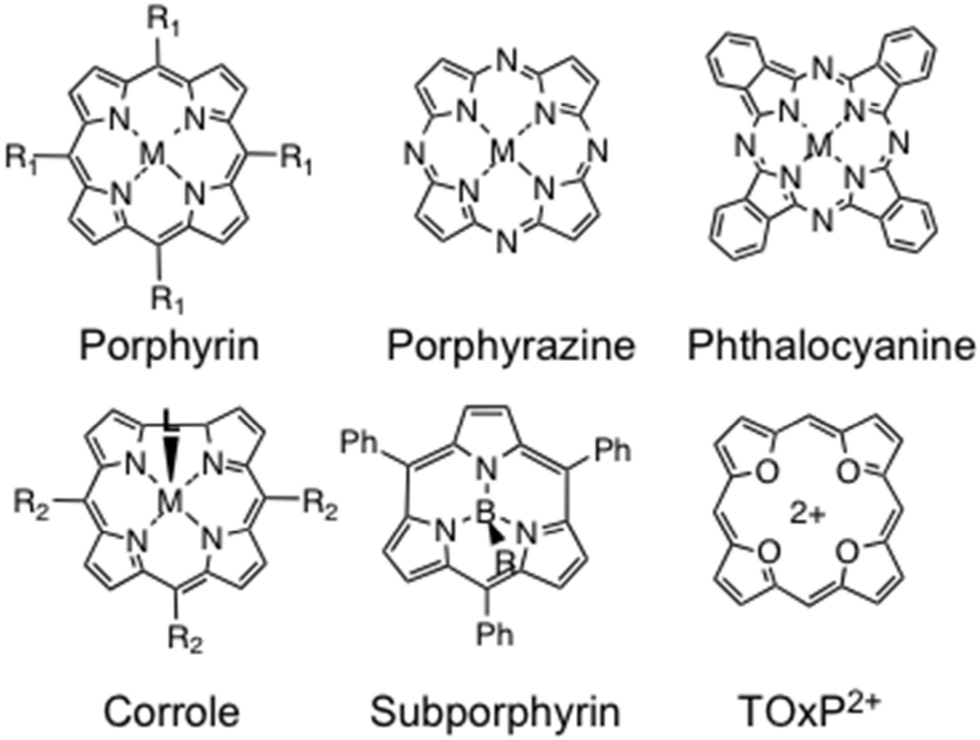
Scheme I:



Scheme 1: Structures of the porphyrinoids considered.

Figures:

Figure 1:

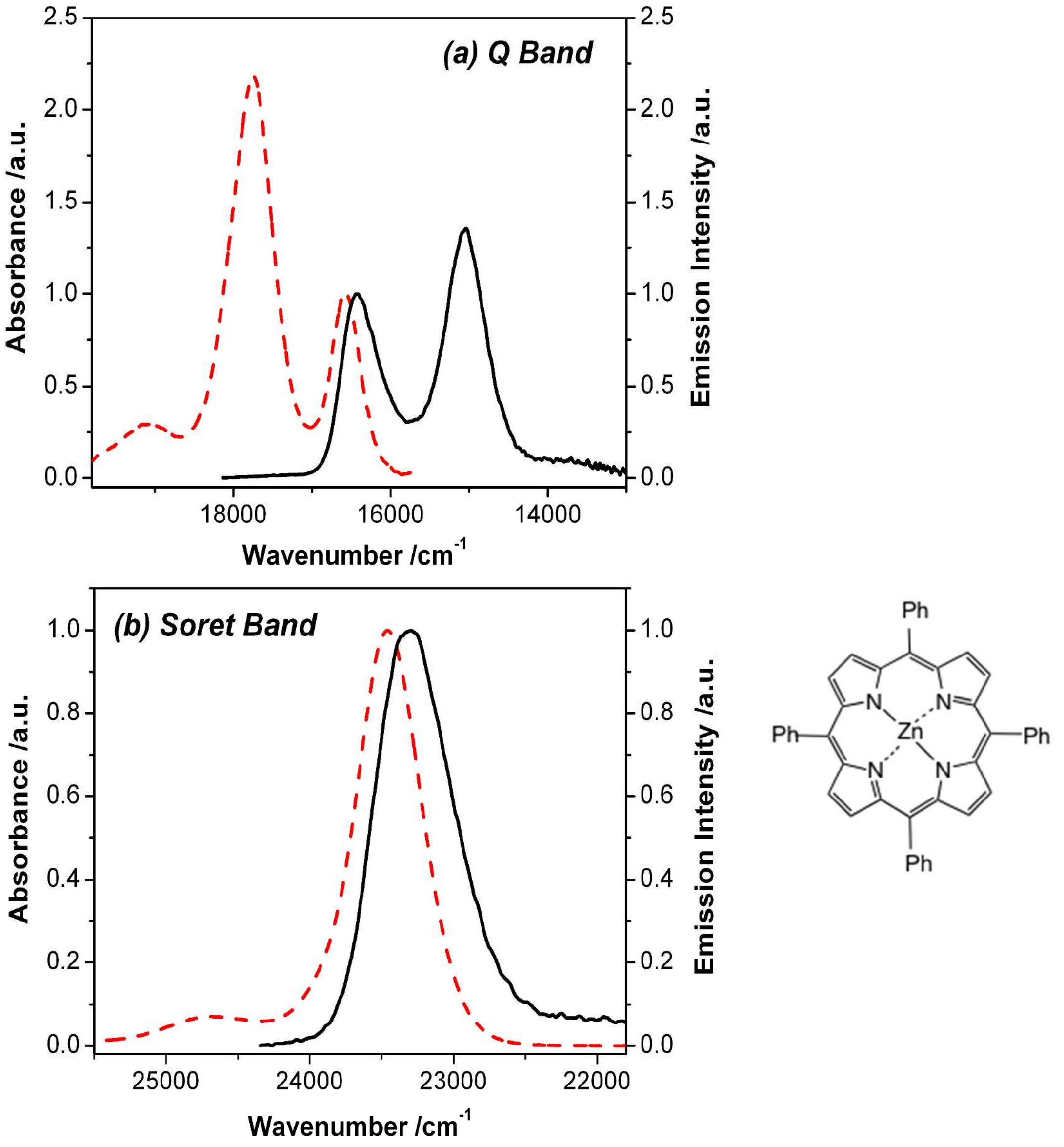


Figure 1: Absorption (dashed) and corrected normalized emission (solid) spectra of ZnTPP in toluene showing the mirror image relationships and small Stokes shifts in both the Q band (upper) and Soret band (lower) regions. Reproduced from Ref. 28 with permission of the American Chemical Society.

Figure 2:

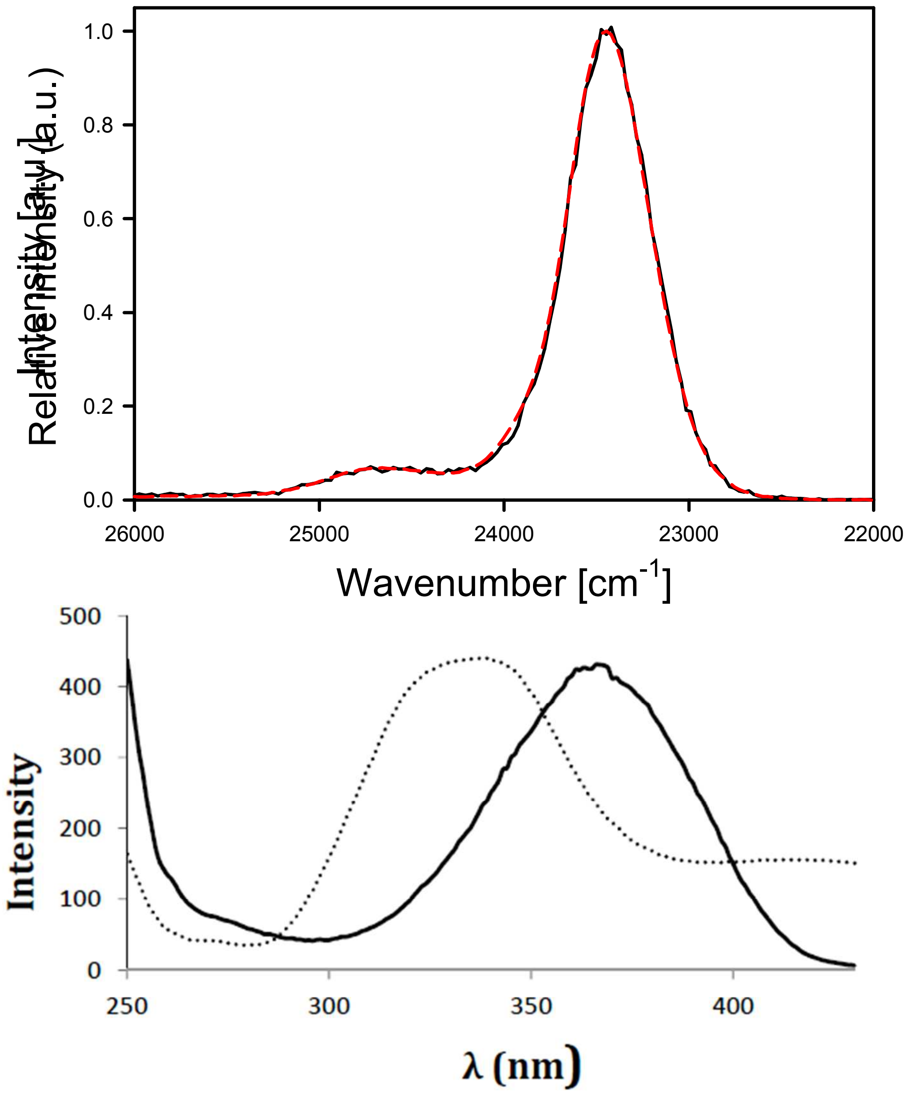


Figure 2. Upper: Overlapping absorption (dashed red) and corrected normalized fluorescence excitation (solid black) spectra of MgTPP in toluene. The excitation spectrum taken by observing fluorescence in the Q band region at 15,000 cm^{-1} (see Figure 1). Reproduced from Ref. 28 with permission of the American Chemical Society.

Lower: Absorption (solid) and corrected normalized fluorescence excitation (dotted) spectra of an impure porphyrazine. The excitation spectrum is taken by observing emission of an impurity, mis-assigned as S_2 fluorescence of the porphyrazine, at the emission maximum of 449 nm. Reproduced from Ref. 18 with permission from the European Society for Photobiology, the European Photochemistry Association, and the Royal Society of Chemistry.