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SPECTROSCOPIC STUDIES OF SOME ZINC MESO-TETRAARYL PORPHYRINS

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SUMMARY

A series of zinc meso-tetraaryl porphyrins (aryl = phenyl, 1'- and 2'-naphthyl, 9'-phenanthryl, and 1'-pyrenyl) has been synthesized and characterised by nmr spectroscopy. The bulky aryl groups are unable to lie coplanar with the porphyrin nucleus and restricted rotation around the C–C connecting bond causes atropisomerism. Photophysical properties of the porphyrins are modulated somewhat by the nature of the aryl group, for excitation directly into the porphyrin nucleus, and although singlet energy transfer occurs from the appended aryl hydrocarbon to the porphyrin it is incomplete for 9'-phenanthryl and 1'-pyrenyl derivatives.

INTRODUCTION

Increasing use is being made of porphyrin derivatives as models for the energy and electron transferring subunits present in natural systems and to explore the possibility of constructing artificial photosynthetic machinery [1]. An important feature of such studies involves the design and synthesis of porphyrin molecules with appended donor or acceptor groups that facilitate rapid transfer of photons or electrons. In order to obtain rates of transfer sufficiently fast that they compete with inherent nonradiative deactivation of the excited states, the positioning of the reactant subunits must be optimised with respect to both separation distance and orientation; it is well established that rates of transfer depend critically upon both parameters [2]. This means that the connecting bridge must be selected with care and it is especially important to avoid flexible linkages that favour adaptation of multiple conformations exhibiting widely different separation distances. The employment of rigid spacer groups to separate donor and acceptor moieties [3] or the use of multiple bridges to connect together single donor-acceptor units [4] overcomes such problems but at the expense of synthetic simplicity.

The difficulty associated with identifying suitable bridges can be avoided by attaching the second molecular subunit directly to the porphyrin ring but this may cause loss of molecular integrity such that it is no longer correct to describe the system in terms of separate subunits. This is a particular problem for electron transfer processes; benzoquinone molecules bonded directly to the porphyrin ring do not retain the characteristic properties of a simple quinone but the whole entity functions as a modified porphyrin, as demonstrated by pulse radiolytic reduction studies [5]. However, this situation should be beneficial for energy transfer processes in which donor groups are bound to a porphyrin acceptor. In this paper we describe the photophysical properties of a few zinc tetraaryl porphyrins in which rapid energy transfer occurs from the aryl hydrocarbon substituent to the porphyrin.

Related systems have been studied before. Thus, zinc(II) tetraphenylporphyrin 1, and its numerous derivatives, has been known for a very long time [6] and it has been characterised in great detail. The phenyl group has been replaced with 1'-naphthyl [7,8], 1'-anthryl [9], 9'-anthryl [7], and ferrocenyl [10] groups whilst the pyrrole rings have been extended to generate benzoporphyrins [11], phthalocyanines [12] and naphthalocyanines [13]. Recent studies have enlarged the central cavity by forming sapphyrins [14] and texaphyrins [15]. In most of these cases the photophysical properties of the porphyrin are changed markedly by the synthetic treatment, often the excited states are pushed to much lower energies. Here, we are concerned with retaining the basic properties of the zinc porphyrin (i.e. the high yield and energy of the long-lived triplet excited state) whilst using appended aryl hydrocarbons to collect high energy radiation and transfer it to the porphyrin moiety. This is a very crude imitation of the natural light harvesting complexes.

EXPERIMENTAL

General

Pyrrole, the various aldehydes, propionic acid and spectroscopic grade solvents were obtained from Aldrich Chem. Co. and used as received. All materials for chromatography were obtained from B.D.H. Chem. and used as received. Absorption and fluorescence spectra were recorded with a Hewlett Packard HP 8450A spectrophotometer and a Perkin-Elmer LS5 spectrofluorimeter respectively, corrected for instrumental responses as necessary. H^1-Nmr and C^{13}-nmr spectra were recorded in $CDCl_3$ solutions using GE QE-300 and GE GE-600 instruments. All compounds gave satisfactory elemental analyses for C, H, N, and Zn on the assumption that the isolated materials were the monohydrates and FAB-mass spectrometry was used to confirm the molecular ions. The assigned structures 1-5 were in full accord with all the spectroscopic data and tlc on silica gel using heptane + CH_2Cl_2 3 + 1 as mobile phase showed the presence of a single component (R_f values: 1 0.28; 2 0.27; 3 0.19; 4 0.23; 5 0.15). Samples were purified by tlc immediately prior to making the spectroscopic measurements.

Materials

Compound 1 was obtained from Midcentury Chem. Co. and purified by column chromatography on alumina using $CHCl_3$ as eluant and subsequently recrystallised from hexane + CH_2Cl_2. Zinc(II) meso-tetra(1'-naphthyl) porphyrin 2 was prepared and purified by the method of Abraham et al. [8]. Zinc(II) meso-tetra(2'-naphthyl) porphyrin 3 was prepared as for 2 and recrystallised from hexane + CH_2Cl_2. Zinc(II) meso-tetra(9'-phenanthryl) porphyrin 4 and zinc(II) meso-tetra(1'-pyrenyl) porphyrin 5 were prepared and purifed by the general method established by Treibs and Haeberle [7]. With all these compounds, extensive column chromatography on silica gel using heptane + $CHCl_3$ was employed to remove residual traces of aryl hydrocarbon.

Methods

Absorption and fluorescence spectra were recorded for extremely dilute solutions of 1–5 in cyclohexane and fluorescence quantum yields were determined relative to 1 ($\emptyset_f$= 0.033) [16]. Singlet excited state lifetimes were recorded for the above solutions using a mode-locked Nd-YAG synchronously-pumped cavity dumped dye laser using Rhodamine 6G as dye and the output was analysed by the time-correlated single photon counting technique. Flash photolysis studies were made with a Q-switched Quantel 481 Nd-YAG laser using 532, 355 and 266 nm excitation as appropriate. Solutions were adjusted to possess an absorbance of ca. 0.1 at the excitation wavelength and were bubbled with N_2. Laser intensities were attenuated using crossed-polarisers and the reported data were obtained at low intensity. Triplet extinction coefficients were obtained by the complete conversion method.

RESULTS AND DISCUSSION

Structural information

X-Ray data collected [17] for crystalline 1 show that the zinc(II) ion in the square-pyramidal configuration is displaced by ca. 0.2Å from the basal plane of the N-atoms towards the coordinated water molecule at a distance of ca. 2.20Å. Steric repulsion between the pyrrole and ortho phenyl H-atoms prevents the meso-phenyls from becoming even approximately coplanar with the porphyrin ring; a situation considerably aggrevated by substitution at the ortho position of the phenyl ring [18]. In the solid state, the meso-phenyls lie at an angle of ca. 60° to the plane of the porphyrin ring and calculations [19] have suggested that the groups are only slightly more coplanar in solution. Despite this obvious nonequivalence of ortho and meta H-atoms on the phenyl rings, the nmr pattern observed for 1 in $CDCl_3$ solution at 300K is remarkably simple. The H^1-nmr spectrum can be interpreted easily, values of 8.95, 8.24, 7.78 and 7.73 ppm downfield of TMS are attributed to C_2 and C_3, ortho-, meta- and para- phenyl protons respectively, and in the C^{13} spectrum all seven C resonances can be observed; C_1 and C_4, C_2 and C_3, C_5, ortho-, meta-, paraand quartenary phenyl C atoms are observed at 150.2, 132.0, 121.1, 142.8, 134.4, 126.5, and 127.5 ppm respectively. The observed averaging of the apparently nonequivalent signals can arise either from rotation around the meso C–C bond or axial ligand exchange occurring on the nmr timescale; systematic studies [18] carried out with various substituted tetraphenylporphyrins indicate that rotation around the meso C–C bond is to be expected in 1. Thus, the phenyl groups in 1 can be regarded as being dynamic.

With 3, where the naphthyl substituent is connected to the meso C atom at the 2'-position, the nmr pattern remains simple and a single set of resonances is observed (Figure 1). In the H^1-nmr spectrum, six clear signals were resolved; the C_2 and C_3 protons being easily recognized at

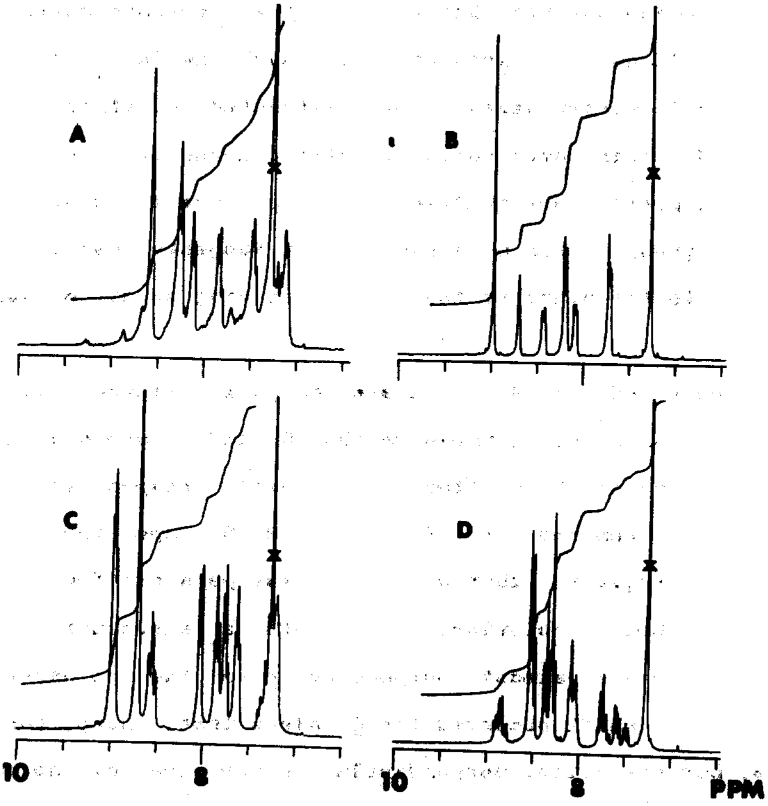

Figure 1. H^1-nmr spectra recorded for (a) 2 (b) 3 (c) 4 and (d) 5 in $CDCl_3$ solution.

8.96 ppm. The naphthyl protons were assigned on the basis of C_{1}', C_{3}', C_{4}', C_{5}' and C_{8}', and C_{6}' and C_{7}' protons being located at 8.69, 8.41, 8.09, 8.19, and 7.70 ppm respectively. In the C^{13}-nmr spectrum, all thirteen signals were resolved with the C_{1} and C_{4}, C_{2} and C_{3}, and C_{5} signals being located at 150.4, 133.4, and 121.1 ppm respectively. The ten naphthyl C signals were tentatively assigned as 140.3, 132.7, 132.6, 125.7, 128.0, 128.4, 126.5, 126.9, 132.1, and 132.2 ppm for C_{1}' to C_{10}' respectively. The relative simplicity of these patterns infers that atropisomerism does not occur in 3 due to rotation around the C–C linkage.

In marked contrast, the nmr patterns observed with 2, where the naphthyl substituent is connected via the 1'-position, are complex (Figure 1). The corresponding spectra obtained for the free-base analogue of 2 remained simple [8] and were interpreted. Such findings infer that 2 demonstrates atropisomerism because of restricted rotation around the bridging C–C bond. This hypothesis is strengthened by the observation that the C_{2} and C_{3} protons are shifted to 8.56 ppm due to shielding by the adjacent naphthyl group. This shielding effect suggests that the naphthyl groups are angled to the plane of the porphyrin ring so as to overlay the pyrrole group.

Nmr spectra recorded for 4 and 5 are complex (Figure 1). In the H^{1}-nmr spectra, signals attributable to the C_{2} and C_{3} protons are split and, and in the case of 5, shifted upfield with respect to 1 and 2; the signals being centred at 8.95 and 8.80 ppm for 4 and 5 respectively. This suggests that atropisomerism persists for both 4 and 5 but that, in $CDCl_{3}$ solution, 4 adopts a structure with the phenanthryl substituents almost perpendicular to the porphyrin ring. The magnitude of the shift observed for 5 infers that, here, the pyrenyl group is close, but not quite, perpendicular to the plane of the porphyrin ring. These suggested structures for 4 and 5 have not been confirmed by X-ray diffraction results but such studies are planned.

C^{13}-Nmr spectra recorded for 2, 4 and 5 in $CDCl_{3}$ solution could not be interpreted fully but the C_1 and C_4, C_5, and bridging substituent C signals were resolved in each case. The observed shifts were consistent with the structures suggested on the basis of the H^1-nmr spectra.

Excitation into the porphyrin absorption bands

In common with the other compounds, the absorption spectrum recorded for **4** in dilute cyclohexane solution (Figure 2) shows three regions of interest; namely, the series of Q-bands located between 480-600 nm, the intense B-band located at ca. 420 nm, and the UV region containing bands associated with the aryl hydrocarbon substituent and weak N- and L-bands arising from the porphyrin ring. The Q- and B-bands refer to excitation into the first and second excited singlet states of the porphyrin molecule respectively and their location and intensity are affected by the nature of the aryl substituent. Spectroscopic details are collected in Table 1.

It is seen that as the number of aryl rings on the substituent (n) increases the B- and Q-bands move towards lower energy, the energy gap between B- and Q_2-bands decreases, the molar extinction coefficient of the

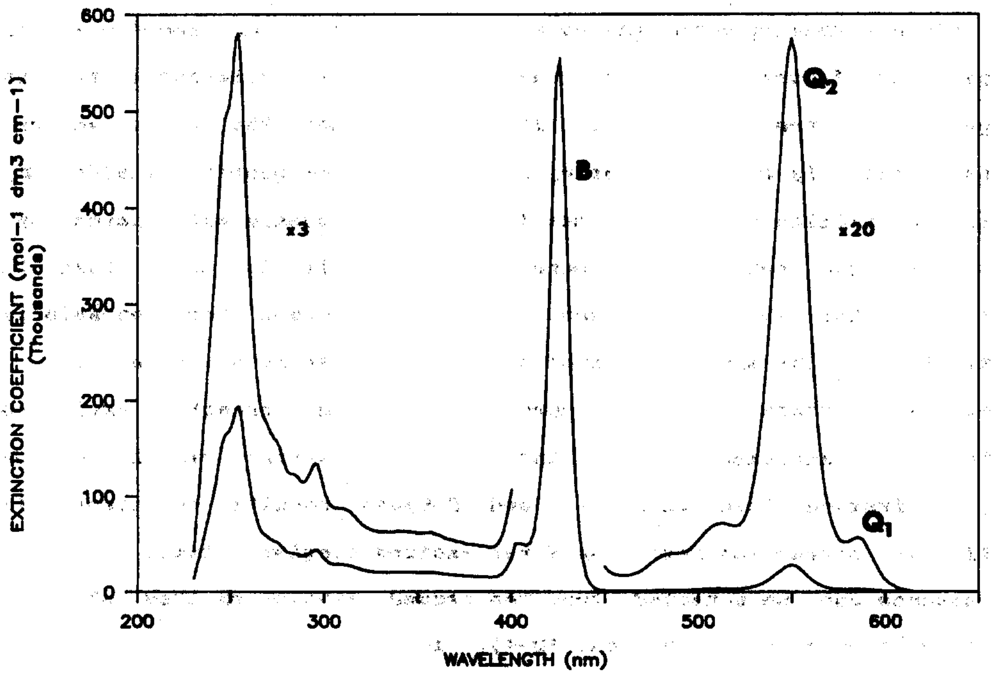

Figure 2. Absorption spectrum of **4** in cyclohexane solution.

B-band decreases whilst that of the Q_2-band increases, and the half-width of the B-band increases. These spectral changes indicate that the larger aryl hydrocarbon substituents induce increased mixing between the two singlet states of the porphyrin molecule. It appears that as π increases the S_0–S_1 transition, which is only partially allowed because of parity restrictions, steals intensity from the more favourable S_0–S_2 transition.

Table 1. Absorption spectral details for 1–5 measured in dilute cyclohexane solution.

cmp	n	λ (nm)	ε (M^{-1} cm^{-1})	λ (nm)	ε (M^{-1} cm^{-1})	λ (nm)	ε ($M^{-1}cm^{-1}$)
1	1	416	597,000	546	22,700	584	2,900
2	2	422	589,000	548	23,500	584	2.020
3	2	424	568,600	550	23,190	590	5,580
4	3	426	554,900	550	28,740	586	2,890
5	4	432	421,900	552	31,270	590	4,650

The fluorescence profiles, measured in dilute cyclohexane solution, show good mirror-symmetry with the corresponding absorption spectra in the Q-region and fluorescence rate constants (k_f) were calculated from the integrated spectra (Table 2). It is seen that the radiative rate increases slightly with increasing n. Fluorescence quantum yields (ϕ_f) and singlet excited state lifetimes (τ_s) also increase with increasing n and, here, the changes are more pronounced; it is clear that the substituent has more effect upon the rate constant for nonradiative deactivation of the singlet excited state (k_{nr}) than it has upon k_f.

For 1–5, there is good agreement between corrected excitation spectra and absorption spectra throughout the entire visible region. Thus, excitation into both Q- and B-bands results in essentially quantitative conversion into the first excited singlet state. Very weak fluorescence can be detected from the second singlet excited state but this is a minor process (ϕ_f = ca. 10^{-4}). In addition, excitation into the B-band gives rise to some hot fluorescence around 570 nm but, again, this is not an important process.

Triplet difference spectra were recorded for 1–5 in N_2-purged cyclohexane for excitation at 532 nm. The apparent maxima in the difference spectra were found to depend upon the nature of the aryl substituent, occurring at 470, 484, 475, 487, and 472 nm respectively for 1–5, but the actual spectral profiles remained similar to those published for 1 [20,21]. Triplet lifetimes remained independent of the substituent and were ca. 0.25 ms; this limit being set by the level of residual oxygen remaining in the solution. At high laser intensity, the triplet state decayed via second order kinetics due to triplet – triplet annihilation; the bimolecular rate constant for this process being (2.5 ± 0.5) x 10^9 dm^3 mol^{-1} s^{-1} for 1–5. Molar extinction coefficients determined at the absorbance maximum for each compound fell within the range (74,000 ± 10,000) M^{-1} cm^{-1} but were characteristic of n. Using the experimentally determined values and with 1 as standard [22], quantum yields for formation of the triplet state (ϕ_t) were measured (Table 2). It is seen that the triplet yields remain similar to that of 1; certainly there are no marked decreases in the efficiency for formation of the triplet manifold as the size of the aryl substituent is increased.

Table 2. Photophysical properties measured for 1–5 in N_2-purged cyclohexane solution.

cmp	n	k_f (10^{-7} s^{-1})	k_{nr} (10^{-8} s^{-1})	τ_s (ns)	ϕ_f	ϕ_t
1	1	1.7	5.2	1.86	0.033	0.83
2	2	1.9	3.7	2.55	0.064	0.81
3	2	1.9	2.3	4.08	0.089	0.81
4	3	2.0	1.9	4.77	0.103	0.89
5	4	2.5	1.9	4.62	0.102	0.85

The most significant change that accompanies replacement of the meso-phenyl group with a larger aryl hydrocarbon is the increase in the fluorescence yield. This increase is due to an increase in k_f, associated with the absorption spectral changes described earlier, and a decrease in k_{nr}. Since the efficiency for formation of the triplet state is not seriously changed throughout the series, despite the decrease in k_{nr}, it appears that the rate of internal conversion from the first excited singlet state must be decreasing. For 1, internal conversion accounts for some 14% of the photon balance but for 4 and 5 it is reduced to a negligible amount. Normally, internal conversion occurs via vibrational relaxation through high energy modes (e.g. pyrrole C-H bonds) and any factor affecting these modes can modulate the efficiency of internal conversion. Orbitals on the large aryl hydrocarbons come into close proximity with the pyrrole H atoms and, probably, affect their ability to dissipate electronic energy via vibrational degrees of freedom. Even allowing for decreased rates of internal conversion, there is also a decrease in the rate of intersystem-crossing upon replacement of the phenyl group and this must relate to symmetry changes induced by the porphyrin nucleus accommodating the larger meso-substituents.

For 1-4 the quantum yields for formation of the triplet state were essentially identical for excitation at 532 or 355 nm. Both wavelengths correspond to excitation into the porphyrin nucleus and, although there are minor losses in photons due to hot fluorescence, it appears that relaxation to the first excited singlet state predominates. For 5, excitation at 355 nm resulted in less efficient formation of the triplet state ($\phi_t = 0.69$) with respect to excitation at 532 nm. Here, the pyrenyl group absorbs at 355 nm, but not at 532 nm, and it would appear that internal transfer of electronic energy from the substituent to the porphyrin ring is incomplete.

Excitation into the aryl hydrocarbon bands

For 1-5 excitation with a laser pulse at 532, 355, or 266 nm gave rise to identical triplet difference spectra, in no case was there any indication of a triplet state being localised on the aryl hydrocarbon [23]. Only for 5, where the aryl substituent absorbs at longer wavelength, did the triplet yield decrease for excitation at 355 nm relative to 532 nm. Attempts to measure triplet yields for 266 nm excitation gave inconsistent results and, in order to evaluate the efficiency of internal energy transfer, fluorescence excitation spectra were recorded.

These spectra were normalised at the Q_2 peak and agreement between fluorescence excitation and ground state absorption spectra remained excellent in the range 370–800 nm. In the UV region, however,

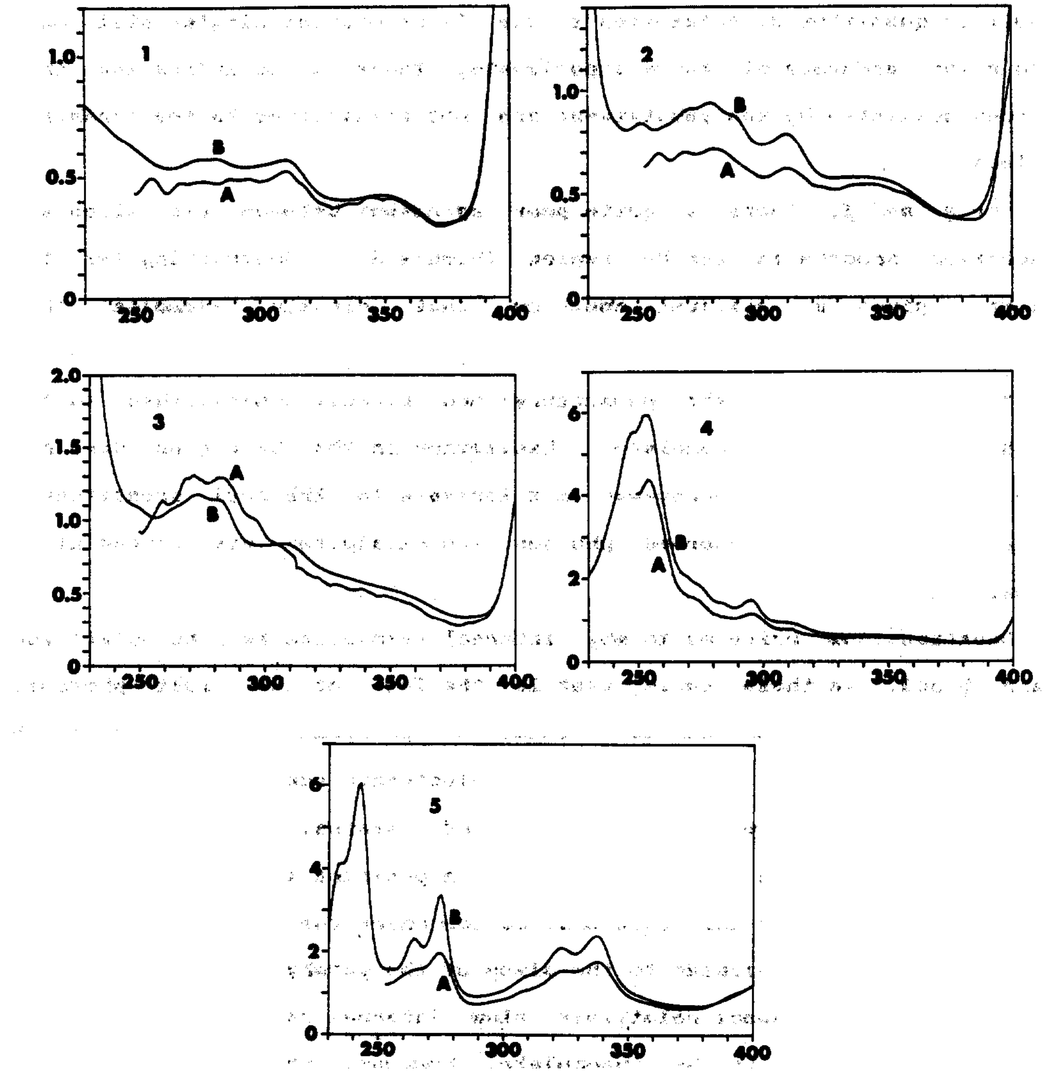

Figure 3. (a) Fluorescence excitation and (b) ground state absorption spectra recorded for 1–5 in dilute CH_2Cl_2 solution.

discrepancies appeared (Figure 3). For 1–3 the discrepancy was quite minor, at least down to 250 nm, and might reflect incomplete correction of the excitation spectra. For these compounds, the absorbance observed between 250–370 nm corresponds to N- and L- transitions localised on the porphyrin nucleus and to (π, π^*) transitions associated with the aryl substituent. It appears that excitation into the N- and L-bands does not result in quantitative relaxation to the first excited singlet state but, within the accuracy of these experiments, there is no indication that photons collected by the substituent are not transferred to the porphyrin nucleus.

For 4 and 5, there is quite poor agreement between excitation and absorption spectra in the UV region (Figure 3). Subtracting the two spectra gives a residual spectrum that closely resembles that characteristic of the aryl hydrocarbon, inferring that transfer of excitation energy from the phenanthryl and pyrenyl substituents to the porphyrin nucleus is incomplete. Excitation in the UV region does not produce high energy fluorescence attributable to the aryl substituent, indicating that the absorbed photons are dissipated via nonradiative relaxation.

Questions now arise as to why internal relaxation is incomplete for 4 and 5 and, in these cases, what is the fate of the "lost" photons. The rate of relaxation can be related to the Fermi golden rule which expresses the rate as the product of an electronic coupling term (V) and the Franck Condon weighted density of states. Changes in the stereochemistry of the molecule will have a profound influence upon V and it seems probable that this term will be low where the aryl substituent is held virtually perpendicular to the plane of the porphyrin ring. Thus, it is reasonable to expect relatively slow internal relaxation in 4 and 5. For relaxation to be incomplete, however, there must be some competing fast nonradiative process that couples the reactant state to the ground state. The details of this coupling process is unknown but will be further investigated using metallo derivatives of 5.

During this work it was noted that excitation at high energy in the presence of halogenated solvents caused oxidation of the porphyrin ring. This is a wavelength dependent reaction, probably involving a CTTS transition, but it is not the origin of the incomplete internal relaxation observed here.

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