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Probing the electronic structure of β,β'-fused quinoxalino porphyrins and tetraazaanthracene-bridged bis-porphyrins with resonance Raman spectroscopy and density functional theory

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HIGHLIGHTS

- The electronic properties of a series of fused porphyrin systems are studied.
- TDDFT and resonance Raman spectroscopy are used to evaluate the nature of the electronic transitions.
- The structural changes that occur upon photoexcitation are quantified using wavepacket theory and the degree of charge localisation to the linker group established.

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ABSTRACT

A number of π-extended porphyrins and bis-porphyrins were characterised by resonance Raman spectroscopy and density functional theory (DFT) calculations, using both B3LYP and CAM-B3LYP functionals. Single porphyrin species, incorporating a β,β'-fused quinoxalino unit, and tetraazaanthracene-bridged bis-porphyrins were investigated. Geometry optimisation predicted all species were planar with respect to the porphyrin core(s). Comparison of experimental with simulated vibrational spectra, obtained via DFT calculations [B3LYP/6-31G(d)], verified the modelling; demonstrated by a mean absolute deviation (MAD) between experimental and calculated band positions of less than 10 cm^{-1}. Simulated electronic transitions obtained via time-dependent DFT [TD-DFT, B3LYP and CAM-B3LYP/6-31G(d)] lay within 0.4 eV of experimental bands and calculations showed perturbation of the frontier molecular orbitals (FMOs) following substitution of the porphyrin core. The nature of transitions that were investigated experimentally via resonance Raman enhancement showed consistency with the character of calculated transitions. A wavepacket analysis of the resonance Raman intensities provided electronic parameters, such as reorganisation energy, as well as normal mode displacements (Δ_i) that were also consistent with the nature of the specific vibrational modes and probed optical transitions. The largest vibrational reorganisation value obtained was for the B_{sh} band of compound (1). This result is consistent with the greater electron density shift of the transition found from DFT and resonance Raman and also the less symmetrical nature of (1).

1. Introduction

Porphyrins have attracted a great deal of interest in the literature due to their rich synthetic chemistry and potential applications [1–6]. They are able to be modified in a number of ways, leading to a class of compounds with diverse optical properties that may be tuned. These properties, arising from the nature of the excited state, include broad absorptions over the visible spectrum and long lived charge separation [7]. Due to these characteristics porphyrins have been suggested as promising candidates as dyes in dye sensitised solar cells [2] and as molecular wires in the form of oligoporphyrins [3–6]. As sensitiser dyes, β-substituted porphyrins have been shown to come close to rivalling the most efficient ruthenium polypyridyl systems [8]. Recently they have also been investigated as sensitisers in triplet–triplet upconversion rubrene systems [9].

The characteristic electronic absorption spectra of porphyrins may be rationalised using Gouterman's 'four-orbital model' [10]. The highest symmetry porphyrins, unsubstituted metalloporphyrins, exhibit D_{4h} symmetry and in the ground state this results in two near degenerate OMOs (a_{1u} and a_{2u}) and two degenerate UMOs (e_g, x and y polarised). The formation of the B and Q states derives

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from a configuration interaction of the electronic transitions between these frontier molecular orbitals (FMOs). The additive configuration gives the intense B band $((a_{2u} \rightarrow e_g) + (a_{1u} \rightarrow e_g))$ which is consequently the higher energy transition of the two, while the weaker, lower energy Q band is formed from the subtractive configuration $((a_{2u} \rightarrow e_g) - (a_{1u} \rightarrow e_g))$. Perturbation of the FMOs arises from substitution of the porphyrin core and the resulting symmetry breaking. Mixing of appropriate substituent and porphyrin MOs also leads to new FMOs allowing further electronic transitions [2].

Considerable effort has been devoted to understanding the structures and electronics of oligoporphyrin systems by Crossley and Reimers et al. [3–6]. This has been realised through a number of computational and experimental methods, including cyclic voltammetry and UV–vis spectroscopy [11], as well as development of techniques to predict the energies of arbitrary oligoporphyrins. The effect of the isomerisation of the porphyrin inner hydrogens has also been investigated [3].

Somewhat less consideration has been given to Raman spectroscopy with regard to these compounds. FT-Raman spectra can be used to verify the accuracy of calculations but perhaps more interestingly *resonance* Raman spectroscopy can be used to elucidate excited state structure and hence add to the understanding of these systems properties. Specifically, using a time-dependent wavepacket analysis of the resonance Raman spectra the resulting normal mode displacements, Δ_i, allow the excited state structure to be mapped out on a mode by mode basis.

The compounds studied are shown in Fig. 1. They vary in the number of porphyrin cores included; being either mono- (with a β,β'-fused quinoxalino group) or bis-porphyrinic (with a bridging 1,4,5,8-tetraazaanthracene moity) in nature and the inclusion of a Sn atom in the porphyrin core(s). This paper uses computational chemistry, resonance Raman spectroscopy and wavepacket modelling to elucidate the structural changes of these species following

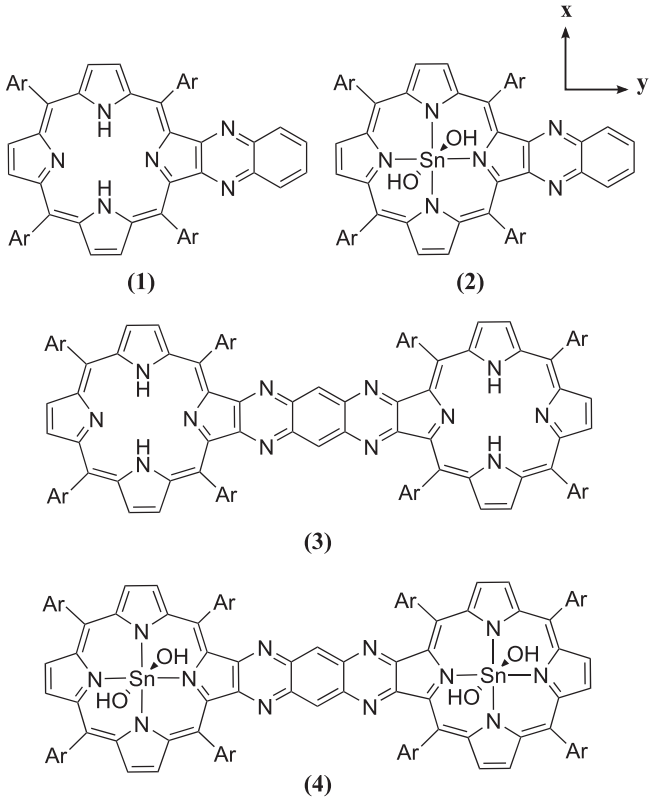

Fig. 1. Schematic of the compounds investigated in this project, Ar = 3,5-Bu$^t_2$C$_6$H$_3$.

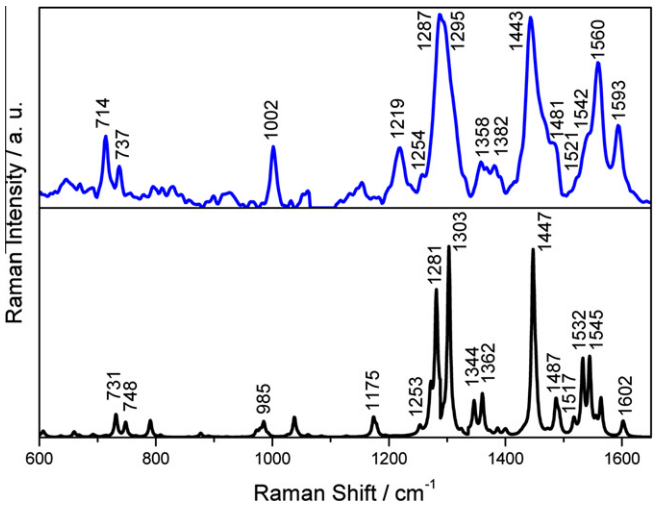

Fig. 2. Experimental FT-Raman spectrum (top trace) of a solid sample of the free-base bis-porphyrin (3) ($\lambda_{ex} = 1064$ nm) and simulated Raman spectrum (bottom trace) obtained from B3LYP/6-31G(d) DFT calculations. The band at 1303 cm^{-1} is significantly overestimated and has been scaled by half in the simulated spectrum.

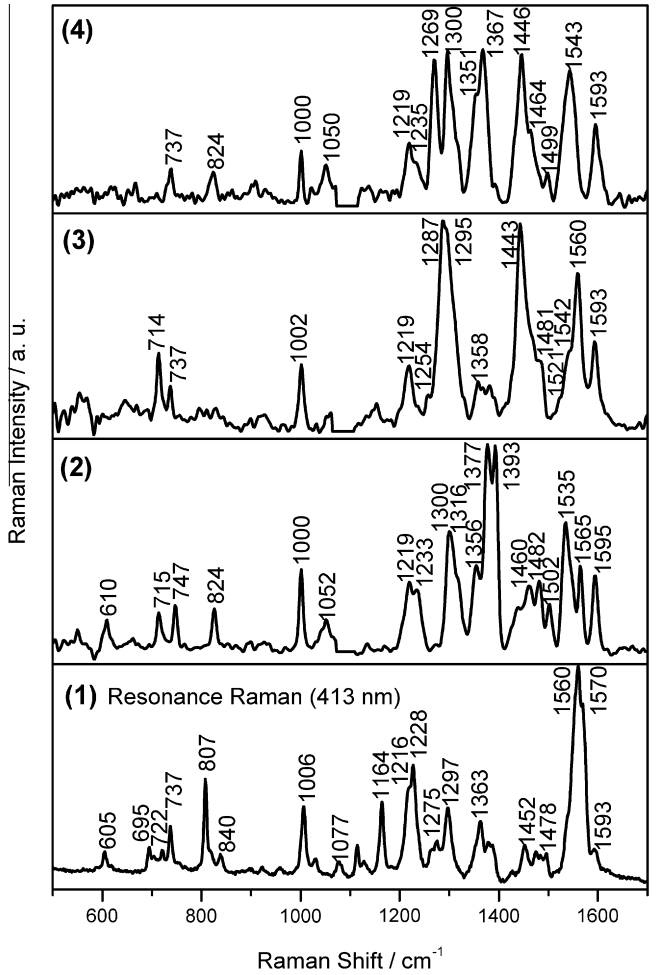

Fig. 3. Experimental FT-Raman spectra ($\lambda_{ex} = 1064$ nm) of solid samples of compounds (2), (3) and (4). The FT-Raman spectrum of (1) could not be obtained due to emission at this excitation wavelength, consequently its resonance Raman spectrum ($\lambda_{ex} = 413$ nm) is used for comparison.

different electronic transitions. This will assist in the understanding of these materials electronic properties and may assist in rational design of further species.