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Abstract

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Keywords

metalloporphyrins, dye, spectroscopic, sensitized, thiophene, solar, cell, dyes, study, dft, substituted

Disciplines

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A spectroscopic and DFT study of thiophene-substituted metalloporphyrins as dye-sensitized solar cell dyes†

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A combination of density functional theory calculations, electronic absorption and resonance Raman spectroscopy has been applied to a series of β -substituted zinc porphyrins to elucidate how the substituent affects the electronic structure of the metalloporphyrin and assign the nature of electronic transitions in the visible region. The use of conjugated β substituents invokes a large perturbation to both the nature and energy of the frontier molecular orbitals and results in the generation of additional molecular orbitals from the parent metalloporphyrin species. A complicated electronic absorption spectra is observed which can be rationalised by an extension of Goutermans' four-orbital model. The excitations involved in the visible transitions have been determined using resonance Raman spectroscopy. This has revealed that the B band retains much of its original nature and is centred largely on the porphyrin core. Additional electronic transitions invoke population of orbitals localised on the substituent chain. The nature of the electronic transitions depends heavily on the type of β substituent. The results of this investigation question some previously held beliefs for the rational design of metalloporphyrins for dye-sensitized solar cell applications.

Introduction

The increasing global demand for energy and declining natural resources has provoked investigation of alternative forms of energy to fossil fuel combustion. Solar power is an attractive option to this problem, as it imparts almost no negative environmental effects and allows use of the freely available radiation emitted by the sun. Until recently this field of research has been dominated by devices which employ only solid-state, inorganic materials and has been primarily advanced by the semiconductor industry.¹ Dye-sensitized solar cells (DSSCs) were developed by Grätzel and co-workers in the early 1990s² as an alternative to solid-state cells. Since that time a considerable amount of work has been carried out in an effort to improve the efficiency of such cells. The most efficient dyes to date are based on ruthenium polypyridyl systems, where efficiencies of up to 11% have been obtained.³ However, the cost and limited availability of ruthenium, coupled with its undesirable environmental impact has led to investigation of organic based materials for DSSC applications^{4–10}

Porphyrins have a number of desirable properties for use in a DSSC and have attracted a great deal of attention.^{4,9–15} They are able to harvest light over a wide spectral range which is crucial for good DSSC performance.⁹ The long-lived excited

states^{9,16} of porphyrins and efficient electron transfer into the conduction band of TiO_2 ¹⁷ are also properties which make them effective DSSC dyes. The highest recorded overall conversion efficiency (η) of porphyrin-based DSSC is 7.1% under standard global AM 1.5 solar conditions.¹⁰ It has been shown that porphyrins containing conjugated substituents at the β -position display higher efficiencies compared to other substitution patterns.⁴ This has been attributed to arise from an increase in absorbance across the solar spectrum due to the electronic effects of extended conjugation at this position.⁹

The electronic structure and absorption spectra of porphyrin compounds is somewhat complex and is best explained by the 'four-orbital model' developed by Gouterman.¹⁸ Unsubstituted metalloporphyrins (e.g. zinc tetra-phenyl porphyrin, ZnTPP) consist of an 18 electron conjugated macrocyclic core of D_{4h} symmetry. The Frontier Molecular Orbitals (FMOs) consist of two HOMOs (a_{1u} and a_{2u}) of almost degenerate energy and a pair of degenerate LUMOs of e_g symmetry (x and y polarised). Electronic transitions can involve excitation from either of the HOMOs to the degenerate LUMO pair. A strong configuration interaction exists between the $^1(a_{2u}e_g)$ and $^1(a_{1u}e_g)$ configurations and linear combinations of the two configurations result in the observed electronic transitions. The additive combination of the transition dipoles of the configurations gives rise to an intense, high energy ($\sim 23\,800\text{ cm}^{-1}$) B band. A relatively weak Q band of lower energy ($\sim 16\,900\text{ cm}^{-1}$) arises from the subtractive combination of the configurations resulting in the near cancellation of the transition dipole. The nearer the degeneracy of the $^1(a_{2u}e_g)$ and $^1(a_{1u}e_g)$ configurations, the weaker the Q band will appear.¹⁹ Symmetry breaking of the porphyrin core and the inclusion of conjugated substituents breaks the $^1(a_{2u}e_g)/^1(a_{1u}e_g)$ degeneracy, resulting in an increase in Q band strength and a decrease in the B band

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† Electronic supplementary information (ESI) available: Table S1 Ground state FT-Raman vibrational data for all compounds. See DOI: 10.1039/b900988d

intensity.^{12,18,20,21} It is possible to empirically determine parameters which describe the energy and nature of the FMOs. The intensity ratio of Q band to the B band ((Q) : (B) ratio) is often used as a measure of the degeneracy of the $1(a_{2u}e_g)/1(a_{1u}e_g)$ configurations.^{12,18} An increase in (Q) : (B) ratio indicates a decrease in degeneracy often resulting from a splitting of the e_g orbital set.

DFT and time-dependent DFT (TD-DFT) computational methods have been used extensively to gain insight into the electronic effects of differing substituents on the FMOs of ZnTPP.^{12–14,22} TD-DFT (B3LYP/6-31G(d)) calculations of zinc porphine (ZnP), have shown that the FMOs are well separated from other MOs and are the major contribution to the Q and B bands, in agreement with the four-orbital model.²³ In addition to this, the B band also contains a minor contribution from lower lying orbitals.²³ In the case of β substituted porphyrins the extension of the π system is calculated to lower the energy and break the degeneracy of the e_g MOs, due in part from symmetry breaking and differing amplitudes at the β substituted position.¹²

Resonance Raman (RR) spectroscopy is well suited to studying and understanding the electronic character of porphyrin systems. Previous work utilising transient RR (TR^2) to probe the lowest excited state of ZnTPP confirmed that the electronic excitations were limited to the porphyrin core, and did not extend out onto the aromatic substituents.²⁴ Although there has been an extensive amount of research involving RR spectroscopy of metalloporphyrins,^{25–29} few data exist for porphyrins with β substituents.^{11,30} These preliminary results reveal that for simple β substituents the ordering of the FMOs does not change upon substitution and differences in vibrational spectra can be explained largely by symmetry breaking and the inclusion of substituent specific modes.³⁰ Addition of conjugated groups shows a large degree of vibrational mode mixing between the β substituent and the porphyrin core vibrations. This indicates strong orbital coupling between the porphyrin FMOs and the conjugated substituent.¹¹

This paper uses a combination of DFT and RR spectroscopic methods to determine the effect of β substitution on the electronic structure of the compounds displayed in Table 1, as well as assign the nature of the observed electronic transitions. In addition to this, comparisons of electronic structure are made between **Ph** and **1** in an effort to ascertain possible reasons for the poor DSSC efficiencies of the β thiophene dyes. This approach may assist in developing the rational design of porphyrin dyes for DSSC applications.

Methodology

The basic details of synthesis are given elsewhere⁹ and was achieved *via* a series of Wittig reactions, integrated with classical porphyrin forming condensation reactions. The compounds were first formed as their ester derivatives, and then hydrolysed to generate the desired acid.

Geometry optimisations, harmonic frequency and time dependent calculations were performed on all compounds using density functional theory with the B3LYP functional and the 6-31G(d) basis set. No symmetry constraints were

Table 1 Structures investigated in this study. Porphyrin dye **Ph** has been previously reported by Campbell *et al.*⁴

Dye	Structure
Ph	
1	
2	
3	

imposed on any of the structures. A scale factor of 0.960 was applied to all calculated frequencies as previously recommended.^{11,31} All calculations were carried out using the Gaussian 03W computational package.³² Diagrams of the vibrational modes and MOs were generated using the Molden³³ and GaussView 3.09W (Gaussian Inc.) software packages, respectively.

Raman spectra were recorded of powder samples using a Bruker Equinox-55 FT-interferometer bench with a FRA106/5 Raman accessory and utilizing OPUS v5.0 software. A Nd:YAG laser operating at 1064 nm provided excitation and a Ge diode (D418-T) functioning at room temperature was used to collect the scattered Raman photons. Typically 64–1000 scans, at 4 cm^{-1} resolution were taken at 2 mW laser power to prevent burning of the sample.

Resonance Raman spectra were recorded using a setup described previously.^{34–37} Spectra from the ground state were generated *via* excitation with 413.1, 457.9, 488.0 and 514.5 nm laser lines. A continuous-wave krypton ion laser (Innova I-302, Coherent, Inc.) initiated excitation at the 351.0, 406.3 and 413.1 nm wavelengths, while a similar argon-ion laser (Melles-Groït) supplied the 457.5 and 488 nm lines. Separate solid state diode lasers (Crystal Laser) provided the additional 444.0 and 514.5 nm lines. Solutions were typically $10^{-3} \text{ mol L}^{-1}$ in CHCl_3 . Intensities were corrected for self-absorption³⁸ as well as detector throughput and response.

Absorption spectra were recorded at room temperature from 200 to 800 nm ($50\,000\text{--}12\,500 \text{ cm}^{-1}$) on a Varian Cary

500 scan UV-Vis-NIR Spectrophotometer utilising Cary Win UV Scan Application software. Solutions were typically 10^{-5} mol L $^{-1}$ in CHCl $_3$ and contained in a 1 cm quartz cell.

Dye-sensitized solar cell fabrication and photoelectrochemical measurements were performed as described previously without modification.⁹ The current–voltage characteristics were determined through applying an external potential bias across the cell and measuring the photocurrent. The overall performance conversion efficiency, η of the cell is calculated as follows:

$$\eta = J_{sc}V_{oc}ff/I_{ph}$$

Where J_{sc} is the integral photocurrent density, V_{oc} is the open cell voltage, ff is the fill factor of the cell and I_{ph} is the incident light intensity.

Results and discussion

Molecular structure and FT-Raman spectra

β -substituted porphyrins containing thiophene substituents have two possible conformers (assuming a planar conjugated array is to be retained) of similar energy *via* rotation about the ethenyl C=C bond. Steric hindrance between the β substituent and the *meso* aromatic groups favours a decrease in the dihedral angle of the thiophene–porphyrin planes and leads to the *gauche* conformer. Conjugation is favoured *via* the *trans* form of the sp 2 carbons and stabilises to the *anti* conformer. Coplanarity of the thiophene units is also retained, primarily due to electronic factors. Electronic effects dominate over sterics and the *anti* conformer is calculated as the lowest energy conformer. However, steric crowding of the *meso* groups increases the porphyrin–thiophene dihedral angle, thus breaking conjugation between the porphyrin core and the conjugated β substituent. This means that the use of zinc porphine (ZnP) in place of ZnTPP for computational simplicity may not be correctly modelling these systems. As a test case **Ph** was modelled with a ZnP core in an effort to quantify the degree of orbital uncoupling. The DFT result shows a 10% difference in calculated HOMO electron density, with little effect on the remaining FMOs. This greatly affects the calculated vibrational energies and eigenvectors. It is thus important to be cautious of the calculations of these over-simplified systems.

The geometry of each compound was optimised using B3LYP/6-31G(d) and the resulting stationary points characterized to ensure minima.³⁹ Harmonic frequencies and intensities were calculated and compared to experimental data as a further check on the validity of the calculations.

A number of possible conformers of ZnTPP are possible, depending on the (*meso*-phenyl)-porphyrin dihedral angle. Indeed, in recent studies the superior CAM-B3LYP functional was used with the 6-31G* basis. When applied to TPP, no less than four local energy minima which may be populated at room temperature were found⁴⁰ and this has been verified experimentally for metallated derivatives.⁴¹ However, electronic excitations involving porphyrins is localised on the porphyrin core and does not extend out onto the *meso* substituents,⁴² and as such, variation in this structural parameter does not affect

Fig. 1 Experimental (blue —) and theoretical (red --) Raman spectra for **1** (top trace) and **3** (lower trace). The experimental spectrum was taken from a solid state sample (λ_{ex} = 1064 nm), while the theoretical spectrum was calculated using the B3LYP/6-31G(d) DFT method.

the electronic nature of the compounds under study here. We have taken the pragmatic approach by using the lowest energy conformer structure of ZnTPP (C $_{2h}$ symmetry) and appended the β substituents to that structure.

In Fig. 1 we present the experimental and DFT calculated FT-Raman spectra (λ_{ex} = 1064 nm) convoluted with a 5 cm $^{-1}$ FWHM Lorentzian function for the structures **1** and **3**. Compound **2** displays a similar spectrum to that seen for **3** and a full vibrational data table with assignments may be found in the ESI.† As evident from Fig. 1 the calculated spectra show excellent agreement to the experimental data in both peak energy and height. It is evident in comparing spectra of **1** and **3** that as the thiophene chain is lengthened, the spectrum becomes dominated by three bands at $\sim$ 1040, $\sim$ 1450 and $\sim$ 1600 cm $^{-1}$. The first two of these correspond to ‘line D’ and ‘line B’ commonly seen in thiophene oligomers^{43,44} while the peak at $\sim$ 1600 cm $^{-1}$ arises from the ν (C=C) mode of the β ethylene component. Line D corresponds to the fully in-plane symmetric bending mode of the C–H bonds of the thiophenes. Line B is always very strong in thiophene-based oligomers and arises from the symmetric, in-phase ν (C=C) motion of the thiophene units. The dominance of these peaks and the lack of mixing with porphyrin modes indicate a partitioning of the systems into the porphyrin core and the thiophene linker components. High energy porphyrin centred vibrations are still visible in the 1500–1600 cm $^{-1}$ region of **1**, but are almost absent in the spectra of **3**.

Information can be gleaned from the Raman spectra in relation to the electronic nature of the structural components. The energy of the β ethenyl ν (C=C) mode appears around 1600 cm $^{-1}$ for all species, indicating minimal effect of different substituents to this moiety. The electronic effect of adding additional thiophene units is thus short range with respect to changes in the force constants. Line B is useful in determining effects the porphyrin core has on the associated double bond character of the units. Comparison of the energy of line B of **1**,

2 and **3** with the parent thiophene, bithiophene and terthiophene compounds allows this effect to be quantified. Line B appears at 1404, 1446 and 1463 cm^{-1} for thiophene, bithiophene and terthiophene respectively. While for compounds **1**, **2** and **3** they are shifted by +42, -3 and -17 cm^{-1} , respectively, compared to the parent species. This trend may be explained by rationalising two components which affect the energy of this band. Mode mixing of this thiophene mode with in-plane porphyrin vibrations increases the energy due to the associated increase in force constants with more vibrationally active components. In contrast to this is the electronic withdrawing effect of the cyanoacrylic acid binding groups which acts to decrease double bond character across the thiophene chain. This latter effect is constant across the species investigated the only effect which leads to the shift in line B is the degree of mixing with porphyrin modes. Thus as the thiophene chain is lengthened the degree of vibrational mixing is decreased as the shift in line B position changes from a blue to a red shift. The calculated eigenvectors for these modes also supports this interpretation (see ESI†).

Electronic absorption spectroscopy

The electronic absorption spectra of all compounds studied, including the spectrum of ZnTPP are shown in Fig. 2. We have tabulated the salient spectral information in Table 2. The spectra of all species are typical of porphyrins with electron withdrawing β substituents, in that additional transitions are observed along with the Q and B bands seen in metalloporphyrins.^{4,9,11,20,45} A reduction in intensity of the B band by two orders of magnitude relative to ZnTPP is observed. This arises from a greater energy splitting of the $^1(a_{2u}e_g)$ and $^1(a_{1u}e_g)$ configurations. The B band in each of **1–3** is blueshifted $\sim 300 \text{ cm}^{-1}$ relative to **Ph**, with a redshift of $\sim 150 \text{ cm}^{-1}$ for the Q bands. The variation in thiophene chain length shows little effect on the energy of the B or Q bands. This indicates that the accepting orbitals for these transitions are almost entirely porphyrin based and that increased conjugation length shows a modest effect on the energy of these MOs.

Fig. 2 Electronic absorption spectra for all compounds; the spectrum of ZnTPP is also included for comparison. Solution spectra were taken in CHCl_3 at $\sim 10^{-4} \text{ mol L}^{-1}$. Transition labels are given in Fig. 3.

At least two other electronic transitions have been resolved *via* peak fitting of the spectra. The prominent band to the red edge of the B band has been termed the T band, and between this peak and the B band is another transition termed B'. The appearance of additional bands in the electronic absorption spectra of β substituted porphyrins has previously been reported.⁹ However the origin of these transitions has not been assigned. It is likely that the B and B' bands arise from the splitting of the B band of ZnTPP into x and y polarised components due to symmetry breaking at the porphyrin core.²⁰ Peak fitting of the spectra implies that the energy of the B' band is also not strongly correlated to an increase in conjugation along the β chain as its energy does not deviate significantly with differing thiophene length. In contrast, the transition energy of the T band is highly dependent on the nature of the β substituent. Extension of the thiophene chain from **1** to **3** leads to a large (1200 cm^{-1}) redshift in the energy of the T band. The accepting orbital in this transition is thus likely to be almost entirely localised on the β substituent and thus contrary to the nature of the B band.

We have empirically determined values of the (Q) : (B) ratio for all compounds. These are given in Table 2. For reference ZnTPP has (Q) : (B) ratio of 0.005.⁴⁶ Clearly there is a large increase in the (Q) : (B) ratio upon β substitution. This can be rationalised by considering the degeneracy of the e_g orbital set. Substitution at the β position imparts a major perturbation of the e_{gx} orbital with little change to the e_{gy} . This drastically breaks the degeneracy and hence results in the larger (Q) : (B) ratio.

Electronic structure

The calculated molecular orbitals of each system are depicted in Fig. 3. These are consistent with the electronic model proposed by Gouterman,¹⁸ but due to the inclusion of a conjugated β substituent additional orbitals are generated. As seen in Fig. 3, the presence of a conjugated substituent at the β position of ZnTPP significantly perturbs both the energy and the nature of the FMOs. The previously degenerate e_g LUMOs are split in energy. The e_{gx} orbital, which has electron density located on the bound β position, mixes with the substituent MOs to form two non-degenerate unoccupied FMOs. The e_{gy} orbital is not of correct symmetry to mix with the substituent derived MOs, and remains relatively unperturbed as a result.

In Fig. 4 we illustrate the splitting of the previously degenerate e_g LUMO pair (x and y polarised) into three MOs, two of which are mixed with the substituent orbitals. The two mixed orbitals (Mix₁ and Mix₂) are not identical in nature due to their differing contributions from orbitals derived from each of the porphyrin and substituent units. The energies of these MOs and the relative orbital contributions from the linker and porphyrin moieties depend on the nature of the linking group. Mix₁ of **Ph** contains more substituent derived orbital character compared with the porphyrin based e_{gx} orbital. Conversely Mix₂ contains a greater contribution of the e_{gx} derived orbital than from the linker MO. The e_{gy} orbital does not undergo orbital mixing with the linker components and is only slightly perturbed compared to the parent e_{gy} orbital. The appearance

Table 2 The wavelengths, wavenumber and molar absorption coefficients ϵ , for the low energy transitions observed in the electronic absorption spectra of each compound. Assignments have been made of each transition and the notation is explained in the text

Compound	λ/nm	ν/cm^{-1}	$\epsilon/10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$	Assignment	(Q) : (B) ratio
Ph	607	16 475	14.6	Q(0,0)	0.16
	566	17 668	21.5	Q(0,1)	
	480	20 838	97.6(sh)	T(0,0)	
	437	22 882	(sh)	B'(0,0)	
	434	23 042	135.7	B(0,0)	
1	612	16 340	23.7	Q(0,0)	0.15
	566	17 668	26.4	Q(0,1)	
	494	20 231	78.5(sh)	T(0,0)	
	461	21 679	(sh)	B'(0,0)	
	429	23 310	175.0	B(0,0)	
2	611	16 367	26.3	Q(0,0)	0.10
	564	17 731	30.1	Q(0,1)	
	514	19 446	58.1(sh)	T(0,0)	
	469	21 324	(sh)	B'(0,0)	
	430	23 256	173.8	B(0,0)	
3	611	16 367	26.2	Q(0,0)	0.16
	568	17 600	33.6	Q(0,1)	
	524	19 089	48.8(sh)	T(0,0)	
	467	21 430	(sh)	B'(0,0)	
	427	23 419	161.0	B(0,0)

Fig. 3 Calculated MO energies using the B3LYP/6-31G(d) DFT method. MO symmetry labels refer to the MOs of ZnTPP (D_{4h}).

Fig. 4 Molecular orbital diagram of ZnTPP and **Ph**, with corresponding simulated electron density maps calculated with the B3LYP/6-31G(d) DFT method. Molecular states and electronic transitions which arise from combinations of the electronic excitations are included. Energy is not to scale.

of new, readily accessible unoccupied orbitals results in the generation of a new configuration interaction involving the five FMOs and the formation of additional molecular states (B' and T). This extension of Goutermans' four-orbital model¹⁸ can be applied to the electronic structure of any β substituted porphyrin containing conjugated, electron withdrawing groups.

In Fig. 5 we present the MO pictures of the Mix_1 , Mix_2 and e_{gy} orbitals of **1**, **2**, and **3**. It is clear from Fig. 5 that as the thiophene chain is lengthened, the Mix_1 orbital loses a great deal of its e_{gx} character to become almost entirely thiophene based. Conversely, the Mix_2 MO gains e_{gx} character and the amount of mixing with the thiophene MO decreases. The reduction in the amount of e_{gx} MO character within the Mix_1 orbital follows the trend of decreasing orbital energy with longer thiophene chains. The orbital energy of Mix_2 also decreases with increasing length of the thiophene chain, although not to the same extent as Mix_1 , resulting in a gradual separation of the orbital energies of Mix_1 and Mix_2 . This trend

Fig. 5 MO diagrams of the 3 lowest lying unoccupied orbitals for **1**, **2**, and **3** (shown left to right).

may be rationalised by considering the relative energy of the thiophene substituents. As the thiophene chain is lengthened, its conjugation length increases. This lowers the energy of the parent thiophene MO and separates it in energy from the parent porphyrin e_{gx} orbitals. Thus there is less overlap of the thiophene and e_{gx} orbitals. The result is that although the two orbitals still interact to induce the splitting, one orbital of each will contain the majority of the parent MO. Interestingly, in the case of **2** and **3** the Mix_2 orbital energy is lowered to such an extent that it becomes lower in energy than the e_{gy} MO. To our knowledge this is the first example of this occurring in β -substituted zinc porphyrins.^{12,13}

As the thiophene chain is lengthened, the localisation of Mix_1 exclusively on the substituent chain creates an entirely donor–acceptor (D–A) system whereby the dipole of the HOMO–LUMO transition is directed towards the binding unit. The lengthening of the thiophene chain increases the D–A character of the system.

TD-DFT calculations

Time-dependent DFT (TD-DFT) calculations have been previously shown to be effective for the prediction and assignment of electronic transitions in freebase and *meso* substituted porphyrins.^{12,47} However, the absolute energies of calculated transitions often deviate significantly from experimental results.^{48,49} Therefore the comparison between experimental and theoretical results is made qualitatively, rather than quantitatively. The TD-DFT calculations of all structures calculate a number of $\pi \rightarrow \pi^*$ transitions with significant oscillator strength. The results for **Ph** and **1** agree well with the experimental spectra. Excitations are predicted within 0.2 eV and relative intensities are within reasonable agreement. The calculated transitions for **Ph** and **1** are listed in Table 3 and are assigned for the B, B', T and Q bands. The excitation giving rise to the B band involves contributions from the H-2 and H-3 orbitals. This departs from the traditional four-orbital model, but arises from the similar energy of these states to the occupied a_{1u} and a_{2u} orbitals, and their inclusion in the configuration interaction.⁵⁰ For other transitions, calculated excitations only involve contributions from the HOMO and HOMO-1 orbitals,

and are consistent with the Goutermans' four-orbital model. All calculated transitions involve orbital contributions from the e_{gy} MO, except for the B' and Q bands, which is calculated to populate the Mix_1 orbital. The redshift of the B', T and Q bands between **Ph** and **1** is also well predicted.

Based on our empirical observations the T and B' bands were believed to have significant Mix_1 and Mix_2 contributions. The calculations imply a significant contribution of these orbitals to the T and B' states of these compounds. For **1** the assigned B' band is calculated to consist of excitations to the Mix_1 and Mix_2 orbitals. While this is true for the T band, there is also a predicted contribution for excitation to the e_{gy} orbital.

For compounds **2** and **3**, the calculated TD-DFT results are in poor agreement with experiment (see ESI for tabulated data). The most notable discrepancy is the calculation of an intense transition of low energy (16943 and 15406 cm^{-1} for **2** and **3**, respectively) which is absent in the experimental spectra. For both cases this calculated excitation pertains primarily to a HOMO $\rightarrow$ LUMO transition. The LUMO of these compounds is localised primarily on the substituent and the HOMO is primarily porphyrin based with some substituent character (see Fig. 4). The excitation between such orbitals is charge-transfer in nature due to the associated movement of charge and a large transition dipole. TD-DFT using B3LYP functional have been shown to underestimate the energy of charge-transfer transitions in model complexes⁵¹ and in porphyrin type systems.⁴⁸ Dreuw and Head-Gordon suggest that the primary origin of the underestimation of charge-transfer transitions is self-interaction error.⁴⁸ Dreuw and Head-Gordon also found charge-transfer states to have lower energies than the Q states, which is similar to what is observed here. Application of the superior hybrid CIS/TD-DFT approach to the same systems correctly predicted the charge-transfer states to lie between the energy of the B and Q states.⁴⁸ It is therefore likely that a similar situation is occurring here and that either (or both) the B' or T band have charge-transfer characteristics.

Resonance Raman spectroscopy

RR spectra of **Ph** collected using 413 and 488 nm (24 207 and 20 492 cm^{-1}) excitation is shown in Fig. 6. Excitation at 413 nm

Table 3 Calculated transitions, orbital coefficients and assignment to experimental data for **Ph** and **1**. Calculated transitions generated via TD-DFT B3LYP/6-31G(d)

Energy [eV]					
Calc.	Expt.	f^a	ϵ_{rel}^b	Assignment	Excitations (orbital contributions)
Ph					
3.30	2.86	0.72	2.83	B	H-2 $\rightarrow$ L + 1(0.17), H-3 $\rightarrow$ L + 1(−0.15), H-1 $\rightarrow$ L + 2(−0.15)
3.29		0.52			H-3 $\rightarrow$ L + 1(0.22), H-1 $\rightarrow$ L + 1(−0.18), H $\rightarrow$ L + 2(−0.14)
2.75	2.84	0.76	0.84	B'	H-2 $\rightarrow$ L(0.67), H-1 $\rightarrow$ L + 2(−0.14)
2.54	2.58	0.56	1.72	T	H-1 $\rightarrow$ L + 2(0.36), H-1 $\rightarrow$ L(0.28), H $\rightarrow$ L + 1(0.28)
2.20	2.04	0.22	0.76	Q	H-1 $\rightarrow$ L(0.59), H $\rightarrow$ L + 1(−0.32)
1					
3.27	2.89	0.89	2.90	B	H-1 $\rightarrow$ L + 1(0.20), H $\rightarrow$ L + 2(0.17), H-2 $\rightarrow$ L + 1(0.15)
2.60	2.69	0.57	0.79	B'	H-2 $\rightarrow$ L(0.68), H-1 $\rightarrow$ L + 2(−0.13)
2.45	2.54	0.40	1.70	T	H $\rightarrow$ L + 1(0.43), H-1 $\rightarrow$ L + 2(0.34), H-1 $\rightarrow$ L(0.14)
2.11	2.03	0.29	0.80	Q	H-1 $\rightarrow$ L(0.70), H $\rightarrow$ L + 1(−0.18)

^a Calculated. ^b Experimental.

Fig. 6 The RR spectra of **Ph** ($\sim 10^{-3}$ mol L $^{-1}$ in CHCl $_3$) obtained using 413.1 and 488.0 nm (24 207 and 20 492 cm $^{-1}$) excitation, which probes the B and T states respectively.

probes the B band, while 488 nm is in resonance with the T band. The B' band is unable to be probed directly with RR spectroscopy due to the heavy overlap of this transition with the adjacent B and T bands. Excitation of the B band (413 nm, 24 207 cm $^{-1}$) shows the appearance of major Raman bands at 1005, 1073, 1139, 1238, 1362 and 1451 cm $^{-1}$ in concert with those in resonance with the T band (488 nm, 20 492 cm $^{-1}$); 1182, 1422, 1588 and 1617 cm $^{-1}$. All of the major peaks observed in both spectra (except for the bands at 1182, 1588 and 1617 cm $^{-1}$) originate primarily from vibrations centred on the porphyrin core. This is consistent with both transitions involving significant contributions from excitations to porphyrin centred MOs. The appearance of modes pertaining to substituent vibrations at 1182, 1588 and 1617 cm $^{-1}$ also indicate that the involved orbitals have a small portion of substituent derived character.

The RR peak enhancement pattern implies that the B and T bands involve population of porphyrin centred MOs and leads to the conclusion that Mix $_2$ and e $_{gy}$ are the significant orbitals involved in these excitations. However, the enhancement of the $\delta(\text{Ph-H})_{\text{sym}}$ (1182 cm $^{-1}$) mode over other peaks with T band excitation implies that this transition displays significant excitation to the Mix $_1$ orbital.

Fig. 7 shows the RR spectra of **1** collected with excitation at 413.1, 457.5 and 514 nm (24 207, 21 858 and 19 455 cm $^{-1}$),

Fig. 7 The RR spectra of **1** ($\sim 10^{-3}$ mol L $^{-1}$ in CHCl $_3$) obtained using 413.1, 457.9 and 514.5 nm (24 207, 21 858 and 19 455 cm $^{-1}$) excitation, which probes the B, B' and T states respectively.

corresponding to population of the B, B' and T states, respectively. Excitation of the B band shows the appearance of numerous peaks, of which most (1052, 1303, 1438 cm $^{-1}$ being exceptions) can be assigned as porphyrin core vibrations. This reflects the same trend seen with excitation of the B band of **Ph**. The same conclusion is also made as in the previous case; the B band arises from excitation primarily to the porphyrin centred, Mix $_2$ and e $_{gy}$ orbitals. Excitation of the B' band shows clear spectral differences to that of the B band, indicating that there is a substantial difference in the excitations which make up the two transitions. Most striking is the loss of peak intensity at 1080, 1303 and 1503 cm $^{-1}$ and almost complete absence of peaks at 1181 and 1359 cm $^{-1}$. A corresponding enhancement in bands at 951, 1438 and 1601 cm $^{-1}$ is observed. Peaks assigned to thiophene modes appear at 1303 and 1438 cm $^{-1}$, while those at 951 and 1601 cm $^{-1}$ are vibrations associated with the ethenyl C=C moiety. The remaining peaks are assigned as porphyrin centred modes.

Identification of vibrations associated with a particular Mix orbital allows the determination of which MO is involved in each transition. The Mix $_1$ orbital displays an electron density plot typical of the unstable quinoid form of thiophene, while Mix $_2$ MO is the corresponding benzenoid form⁵² (see Fig. 8). The RR bands typically enhanced with population of the quinoid form involve stretches of the double bond at positions 2 and 3.⁵³ The benzenoid form should then show the converse stretch at positions 1–2, and 3–4. Thus it is possible to differentiate excitation to the two MOs based on type of mode enhancement observed across the different transitions. The mode at 1303 cm $^{-1}$ is assigned to a vibration of the thiophene at positions 2–3 and 4–5 relating to the benzenoid form, while the enhanced peak at 1438 cm $^{-1}$ is the stretch between the

Fig. 8 The quinoid and benzenoid form of **1** with the corresponding Mix $_1$ and Mix $_2$ (e $_{gx}$) MOs. Vibrational eigenvectors are calculated with the B3LYP/6-31G(d) DFT method, calculated energies are given in parentheses. Atom numbering of the thiophene unit is included.

2 and 3 positions, and hence indicative of the quinoid thiophene form (see Fig. 8). Both modes also show significant C–H in-plane bend of the thiophene units.

This RR band enhancement pattern is consistent with the B band populating the e_{gy} and Mix_2 orbitals, as both contain significant porphyrin character. The appearance of the peak at 1303 cm^{-1} has been assigned as the vibration of the benzenoid form of thiophene, and as such is indicative of excitation to Mix_2 . B' band excitation consists of increased Mix_1 population and decreased e_{gy} and Mix_2 character, which is expressed as the major loss in porphyrin centred vibrations and the 1303 cm^{-1} peak, with a corresponding gain in intensity of the quinoid thiophene mode at 1438 cm^{-1} .

RR scattering from the T state (514 nm , $19\,455\text{ cm}^{-1}$) gives band enhancement similar to that observed for B' excitation, but with subtle differences. There is an extended loss in intensity of the porphyrin centred modes at 1582 and 1551 cm^{-1} , with a slight gain in the peak at 1052 cm^{-1} and increasing intensity of the 1303 and 1438 cm^{-1} thiophene peaks. This indicates that the T band predominantly arises through excitation to the two Mix orbitals, as both the quinoid and benzenoid thiophene vibrations display band enhancement.

Similar to the previous example is the RR spectra exciting the B, B' and T states of **2** were using 413 , 444 and 514 nm ($24\,207$, $22\,523$ and $19\,455\text{ cm}^{-1}$) excitation, respectively. Excitation of the T band (514 nm , $19\,455\text{ cm}^{-1}$) reveals peaks at 1051 , 1303 , 1443 and 1602 cm^{-1} with few other features. The former peaks are assigned as thiophene centred vibrations, while the 1602 cm^{-1} vibration is the $\nu(\text{C}=\text{C})$ mode. The RR enhancement pattern of T band excitation is consistent with this transition primarily populating the Mix_1 orbital. RR scattering from the B' state (444 nm , $22\,523\text{ cm}^{-1}$) shows the appearance of additional porphyrin centred peaks over that of T band excitation. A slight loss in 1443 cm^{-1} peak intensity and noticeable enhancement of the 1303 cm^{-1} mode is observed. This trend is similar to that seen with **1**, where the benzenoid thiophene vibration (1303 cm^{-1}) is enhanced over the quinoid mode (1443 cm^{-1}). This in turn suggests that the B' band is made up of excitations of all three lowest unoccupied molecular orbitals, with particular contributions from the Mix_2 and e_{gy} orbitals. B band excitation shows an extension of this trend, in that the 1443 cm^{-1} band is further suppressed, with a gain in intensity of the 1303 cm^{-1} band and other porphyrin centred vibrations. This is consistent with the B band transition consisting of excitations almost entirely to the e_{gy} and Mix_2 orbitals.

B band excitation of **3** also differs significantly to that of the other compounds with substantial enhancement of the peaks at 1238 and 1361 cm^{-1} (see Fig. 9) assigned as the $\nu(\text{C}_m\text{--Ph})$ and $\nu(\text{Pyr quarter-ring})$ vibrations. Enhancement of these type of modes with B band excitation implies that the electronic excitations are to orbitals which are entirely centred on the porphyrin core. In this example it is likely that the porphyrin centred e_{gy} and Mix_2 MOs are the accepting orbitals, as these have almost no electron density on the thiophene linker.

Similar to the previous cases, the B' and T bands comprise of excitations to the lower lying unoccupied MOs. The T band consists primarily of population of Mix_1 , while the B' band

Fig. 9 The RR spectra of **3** ($\sim 10^{-3}\text{ mol L}^{-1}$ in CHCl_3) obtained using 413.1 , 457.9 and 514.5 nm ($24\,207$, $21\,848$ and $19\,455\text{ cm}^{-1}$) excitation which probe the B(0,0), B'(0,0) and T(0,0) bands respectively.

contains a minor contribution from the porphyrin centred orbitals. This is reflected in the presence of only two major peaks in the RR spectrum of T band excitation at 1048 and 1453 cm^{-1} . The calculated eigenvector results from the DFT calculations relate both of these peaks to thiophene breathing modes with substantial $\delta(\text{Thio-H})_{\text{sym}}$ character.

DSSC performance

There are a number of properties this series of substituted porphyrins have which make them effective test cases for determining traits desirable for improved DSSC dye performance. As previously discussed, lengthening of the thiophene chain with additional units induces a separation of the unoccupied FMOs and causes Mix_1 to become entirely thiophene based, leaving Mix_2 and e_{gy} primarily porphyrin localised. This is essentially creating a donor–acceptor (D–A) system with the acceptor unit localised on the substituent and a transition dipole directed towards charge injection on the TiO_2 surface. In concert to this, the absorption profile of **2** and **3** shows redshifted absorption bands in the region between the Q and B bands. Combined with a decreased band gap, there should be an increase in solar conversion efficiency across the **1–3** series based on the previous design of photosensitive organic dyes.^{13,14,17,54–56} However this is not the observed trend in these species, as exemplified with the electronic absorption and solar cell data listed in Table 4. There are a number of possible reasons behind the observed efficiency trends, all of which imply that increasing D–A strength (in porphyrin systems) is not a valid methodology to improving dye performance, instead it leads to photo-physical traits which diminish efficiency. Here we discuss some possible theoretical reasons behind the observed trends.

The localisation of FMOs with increasing thiophene length means that Mix_1 (Fig. 5) is the only unoccupied FMO which has much amplitude near the binding moiety of the dye. The other unoccupied FMOs are all porphyrin localised and hence excitation to these orbitals does not lead to effective charge injection due to the distance to the TiO_2 surface. As previously discussed, the only electronic transition with Mix_1 as the major acceptor orbital is the T(0,0) band. Thus any improvement in

Table 4 Total electronic absorption cross-section (arb. units), open circuit voltage (V_{oc} , mV), short circuit current (J_{sc} , mA cm⁻²) and solar power conversion efficiencies (η , %) for all compounds studied

Compound	Total absorption cross-section (arb. units)	V_{oc} (mV)	J_{sc} (mA cm ⁻²)	η (%)
Ph	35.5	530	11.0	3.7
1	18.4	499	4.9	1.2
2	16.1	534	4.2	1.1
3	15.4	537	3.1	1.0

increased D–A strength is transmitted into increase charge injection from only this orbital. However there is another factor which means the T(0,0) band is unable to be effective in energy harvesting. Localisation of Mix₁ primarily on the substituent chain means that there is poor orbital overlap between Mix₁ and the porphyrin localised donor orbitals. This means that the T(0,0) band transition is relatively weak for the strong D–A systems (**2** and **3**, see Fig. 3). Consequently, even though the transition is pushed to the red (a desirable quality for DSSC dyes) the loss in oscillator strength means that the light harvesting efficiency of this transition is diminished.

The light harvesting efficiency of a dye can also be correlated to the total absorption cross-section across solar emission range (this contains a number of assumptions, which will not be discussed). The tabulated data illustrates that the total absorption cross-section drops by half when the phenyl linker (**1**) is substituted with thiophene (**2**), this follows a 50% loss in solar cell efficiency. It is likely that this effect, coupled with problems associated with strong porphyrin D–A systems is the reason behind the poor efficiency of these thiophene substituted porphyrin dyes. Additional factors influencing performance with these, and related dyes are currently under investigation and will be the topic of a further report.

Conclusion

From comparison of the experimental and calculated ground state vibrational spectra, the B3LYP/6-31G(d) DFT method was determined to be an accurate model of all compounds investigated in this study and allowed the calculated electronic structures to be used in the interpretation of experimental data.

The calculated MO energies and electron density plots indicate that the substitution of a conjugated linking group at the β position leads to a splitting of the previously degenerate e_g LUMOs. The e_{gx} and linker orbitals undergo mixing and further split in energy to create three unoccupied orbitals (Mix₁, Mix₂ and e_{gy}) from the original degenerate LUMO pair. Extension of the conjugation of the linking group with increasing thiophene units increased the calculated orbital splitting. The mixing of the porphyrin and linker derived orbitals also decreased resulting in orbitals consisting of either solely porphyrin or thiophene character. This trend is crucial in explaining all of the observed electronic properties.

Electronic absorption spectra show the appearance of at least four electronic transitions for all compounds in the visible energy region (Q, T, B' and B bands) and for the first time the nature of these transitions is assigned. Empirical calculations based on observed data, and resonance Raman spectroscopy indicates that the nature of these electronic transitions varies between the different compounds. As the

thiophene chain is progressively lengthened, the B band tends to involve excitations solely to the porphyrin localised orbitals (Mix₂ and e_{gy}). The B' and T bands primarily populate the thiophene localised Mix₁ orbital, though the B' band retains more porphyrin character than the T state.

It was shown that a longer thiophene chain induces a greater D–A character, decreased band gap and red shifted adsorption bands, but showed decreased solar efficiency. These results are in contrast to previous assumptions on desirable traits for efficient solar conversion and it will be the focus of future work to rationalise DSSC efficiency with electronic properties.

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