Calculation of frontier orbitals, electronic coupling and paramagnetic interaction of conjugated porphyrin arrays based on DFT theory

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Abstract

Electronic donor–acceptor communication in porphyrin-based molecular electronics is addressed theoretically. The order of the a_{1u} and a_{2u} frontier occupied orbitals has been proposed by others to affect excited energy transfer. We examined the effects of the nature and pattern of substituents upon analog monomer porphyrin orbitals using DFT (B3LYP/6-31G(d,p)) and the four-orbital model of porphyrin electronic structure. The excited state energy transfer rate was found to be very sensitive to these orbitals' contributions to porphyrin uv/visible absorptions (B- and Q-band). Ground state homodimer calculations validated the monomer results.

1. Introduction

Molecular electronics has garnered much attention¹⁻². Understanding the electronic communication between a donor and acceptor pair is critical for the rational design of nanoscale molecular electronic devices. Recently, several prototypical molecular electronic elements were made using porphyrins as building blocks.³⁻¹⁵ One key fact is that the ordering of the porphyrin frontier orbitals plays a crucial role in determining the rates of electronic communication.^{2, 16-20, 15} Moreover, the variation in electron transfer rates was proposed to arise from different ordering of the HOMO and HOMO-1 orbitals. For example, high density would be associated with efficient interporphyrin electronic communication, and thus rapid electron transfer. Similar results were found for ground state electron/hole hopping rates in fluorinated and unfluorinated zinc porphyrin homodimers.²¹

The two highest occupied metalloporphyrin orbitals, a_{1u} and a_{2u} , are nearly degenerate, but have substantially different electronic distributions (Fig. 2). The a_{2u} orbital is heavily populated at the meso-carbons but has only slight density at the β -carbons. In contrast, the a_{1u} orbital has virtually no electron density at the meso-carbons but has a large population at the β -carbons. ET photoinduced in resonance with the Q-band

region of the spectrum is dominated by the HOMO (see below). For meso-linked systems, then, having a_{2u} = HOMO should result in faster ET than having a_{1u} = HOMO. The converse should be true for β -linked porphyrins.

In this work, we report upon an investigation of electronic communication in porphyrin dimers employing high-level DFT calculations and the Gouterman four-orbital model. In particular, studies of a series of monomer analogs of the ZnFbU-*m* dimers have allowed a detailed exploration of the effects of the nature and pattern of peripheral substituents decorating the porphyrin macrocycle upon the frontier orbital energies. The relationship between the photoinduced ET rates and the frontier orbital energetics was explored by analyzing the contributions of each of the frontier orbitals to the observed uv/visible absorption transitions. In addition, challenging ground state calculations of homodimer zinc porphyrin systems were performed. Our results account for the experimental findings, and show a correlation between the experimental ET rates and the frontier orbital ordering and magnitude of energetic splitting. More importantly, this study provides a theoretical guideline for the design of porphyrin-based molecular electronics.

2. Methods

All quantum mechanical calculations were full geometry optimizations performed using GAUSSIAN 98W on a PC platform, employing symmetry only where appropriate. The B3LYP hybrid functional and a moderate Gaussian-type basis set (6-31G(d,p)) were used.

One component of this study is the determination of the magnitudes of the contributions of relevant electronic configurations to the uv/visible electronic excitations of the Zn porphyrin: the B-band (~ 400 – 450 nm) and the Q-band (~ 550 – 600 nm) (Fig. 3). These two porphyrin absorption bands involve π – π^* transitions among the frontier orbitals, primarily the a_{1u} and a_{2u} occupied and the e_g unoccupied orbitals. The magnitudes of the contributions depend upon several factors, including the ordering of the frontier molecular orbitals, the energy differences among them, and the configuration interaction (CI) coupling strength. We developed a quantitative model to determine these magnitudes based upon the Gouterman four-orbital picture for porphyrin electronic structures, the eigenvalues associated with the frontier orbitals determined by our DFT calculations, and the experimentally observed absorption spectra, where available.

Fig. 3. Transitions and configuration interaction in the Gouterman four orbital model. (a) Four allowed transitions, $(a_{1u}e_{gx})$, $(a_{2u}e_{gy})$, $(a_{1u}e_{gy})$, and $(a_{2u}e_{gx})$, each with E_u symmetry, mix via configuration interaction. (b) The lower energy doubly degenerate $\text{HOMO} \rightarrow e_g$ transition has a larger contribution to the Q-band, while the higher energy doubly degenerate $(\text{HOMO}-1) \rightarrow e_g$ transition has a larger contribution to the B-band. The absorption spectrum shown is Zn porphine in CS_2 .

The Gouterman four-orbital model assumes that only the $(a_{2u})^1(e_g)^1$ and $(a_{1u})^1(e_g)^1$ configurations participate in the Q- and B-bands (Fig. 3a). Both of these doubly degenerate excited state configurations have E_u symmetry, generating strong CI. Since these configurations are only nearly degenerate, their contributions to the Q- and B-bands are unequal. The lower energy configuration $(\text{HOMO})^1(e_g)^1$ will contribute more to the Q-band, and the higher energy $(\text{HOMO}-1)^1(e_g)^1$ more to the B-band (Fig. 3b). With similar expressions for y-polarized transitions [16], B_x^0 and Q_x^0 are a basis of 50–50 mixtures of the $(a_{1u})^1(e_g)^1$ and $(a_{2u})^1(e_g)^1$ configurations. That is, if the a_{1u} and a_{2u} orbitals are (accidentally) exactly degenerate for the D_{4h} porphyrin, then $B_x = B_x^0$ and $Q_x = Q_x^0$. The unmixing coefficient θ_x that relieves their non-degeneracy. For these initial studies, the two lowest energy LUMOs were assumed to be degenerate, as is strictly true, by symmetry, for D_{4h} porphyrins. Under this assumption, the measured absorption spectrum and B3LYP/6-31G(d,p) energies for the top two HOMOs and lowest two LUMOs are used to calculate the CI coupling strength. The absorption spectrum of $\text{F}_{10}\text{-ZnTPP}$ is not known, therefore a value of $C=3200\text{cm}^{-1}$ was used in the calculating the molecular orbital contributions to the excited state. This value is an average from calculations for species whose absorption spectra are known.

3. Results and discussion

The goal of these studies was to examine the dependence of photoinduced ET rates in porphyrin arrays upon the electronic structure of the system. For porphyrins, the absorption bands used to photoinduce ET derive primarily from strong CI mixing of four electronic excitations involving the occupied a_{1u} and a_{2u} orbitals and the doubly degenerate unoccupied e_g orbitals (Fig. 3). Therefore, these studies began by exploring the energies of these frontier orbitals in monomer analogs of the ZnFbU dimer (Fig. 1).

We focused upon Q-band excitation of the meso-linked systems, though the approach applies equally well to the β -linked dimers and to excitation in the B-band.

The B3LYP hybrid density functional and a moderate, Gaussian-type basis (6-31G(d,p)) were used to perform full geometry optimizations on the set of porphyrins depicted in Fig. 1b. The DFT was employed for several reasons. By their nature, DFT methods address the electron density directly. In fact, unlike Hartree–Fock (HF) theory, the Kohn–Sham (KS) orbitals, in principle, can give the exact ground state electron density. In addition the KS orbitals are based upon a one-electron potential that includes correlation. Hence DFT methods are less expensive (time, memory) than HF-based methods at correlated levels. Finally, the KS orbitals have been recently found to be valuable, and perhaps even better than HF-based molecular orbitals, when used in the molecular orbital picture. Orbital ordering and energy differences are calculated well. In particular, the B3LYP functional, which was parameterized for accuracy in calculating energetic observables, has been widely successful.

Fig. 4, Fig. 5 show some results of B3LYP/6-31G(d,p) calculations on substituted zinc porphyrins. Zn porphine is the simplest zinc porphyrin, with hydrogens at all 12 peripheral sites on the macrocycle. The a_{1u} and a_{2u} orbitals were found to be nearly degenerate in Zn porphine, with a_{1u} the HOMO by only 0.12 kcal/mol (Fig. 4). Upon replacement of the four meso-hydrogens with electron-donating phenyl groups (ZnTPP (**3**)), the a_{2u} orbital was preferentially destabilized, making it the HOMO by 1.7 kcal/mol. Increasing the electron-donating capacity of the phenyls by substitution of $-NH_2$ groups at the *ortho* positions ($(o,o'-NH_2)_8$ -ZnTPP (**4**)) further destabilized the a_{2u} orbital.

Fig. 4. Relative a_{1u} and a_{2u} energies for several substituted zinc porphyrins. (a) Zn porphine; (b) ZnTPP (3**); (c) ZnTPP with $-NH_2$ at phenyl *ortho* positions (**4**); (d) F_{20} -ZnTPP (**5a**); (e) Cl_{20} -ZnTPP (**6**); (f) Br_{20} -ZnTPP (**7**). Full geometry optimizations were performed at the B3LYP/6-31G(d,p) level. The numbers in parentheses are the energies of the a_{2u} orbitals relative to the a_{1u} .**

Fig. 5. Relative a_{1u} and a_{2u} energies for a series of fluorinated ZnTPPs. ZnTPP with 0 (a), 1 (b), 2 ((c) = across macrocycle, (d) = adjacent on macrocycle), 3 (e) or 4 (f) pentafluorinated meso-phenyls (5a–5e). Full geometry optimizations were performed at the B3LYP/6-31G(d,p) level. The numbers in parentheses are the energies of the a_{2u} orbitals relative to the a_{1u} .

The use of electron-withdrawing groups had the predicted effect of preferentially stabilizing the a_{2u} orbital relative to the a_{1u} . By tuning the degree of electron withdrawing power, the ordering and splitting of the frontier orbitals could be easily and nearly continuously altered. For example, by pentafluorinating the phenyl groups in ZnTPP to form F_{20} -ZnTPP(**5a**), the a_{2u} orbital, which was the HOMO in ZnTPP by 1.7 kcal/mol, was stabilized to become the (HOMO-1) in F_{20} -ZnTPP. Using less electronegative halogens reduced the degree of stabilization correspondingly, bringing the a_{2u} orbital closer in energy to the a_{1u} HOMO (Fig. 4).

The splitting and ordering could be tuned by changing number of electron-withdrawing groups as well. For example, the pentafluorophenyl series in Fig. 5 shows a wide range of ordering and splitting from ZnTPP to F_{20} -ZnTPP. Each pentafluorophenyl group additively stabilized the a_{2u} relative to the a_{1u} orbital by approximately 0.85 kcal/mol. ZnTPP and F_5 -ZnTPP (**5e**) had an a_{2u} orbital as the HOMO. With two pentafluorophenyl groups and two phenyl groups (F_{10} -ZnTPP), the a_{1u} and a_{2u} orbitals were nearly degenerate, regardless of whether the pentafluorophenyls were across the macrocycle (**5d**) from each other or at adjacent meso-positions (**5c**). Finally, in F_{15} -ZnTPP (**5b**) and F_{20} -ZnTPP (**5a**) the a_{2u} orbital experienced sufficient stabilization to drop below the a_{1u} .

To understand the influence of the frontier orbitals upon ET, excited state wavefunctions must be explored. The ground state configuration of metalloporphyrins is either $(a_{1u})^2(a_{2u})^2(e_g)^0$ or $(a_{2u})^2(a_{1u})^2(e_g)^0$. The doubly degenerate $(a_{2u})^1(e_g)^1$ and $(a_{1u})^1(e_g)^1$ are the lowest energy π - π^* excitations (Fig. 3a). Both have E_u symmetry, yielding strong CI. The Gouterman four-orbital model assumes that only $(a_{2u})^1(e_g)^1$ and $(a_{1u})^1(e_g)^1$ interact to generate the observed Q- and B-bands. The lower energy configuration (HOMO) $^1(e_g)^1$ will contribute more to the Q-band, and the (HOMO-1) $^1(e_g)^1$ more to the B-band (Fig. 3b). These contributions, in turn, determine the electronic character at the linker carbon upon excitation. The HOMO therefore should dominate the Q-excited ET rates, and the HOMO-1 the B-excited rates.

The size of the contribution of the HOMO or HOMO-1 to the Q- and B-bands depends upon the ordering and energy gap between the a_{1u} and a_{2u} orbitals and the CI coupling

strength. We have used our DFT results and experimental absorption spectra, where available, to quantify the relative contributions of each excited configuration $(a_{1u})^1(e_g)^1$ and $(a_{2u})^1(e_g)^1$ to the Q- and B-band excited states, within the framework of the Gouterman picture (Table 1).

For the meso-linked dimers, Q-excited ET rates should be slow when a_{1u} is the HOMO with a large component contributing to the Q-band, and fast when a_{2u} is HOMO with a large component. Our results support this hypothesis. For example, F_{30} -ZnFbU-*m* has a relatively long ET lifetime of 240 ps. The analog of F_{30} -ZnFbU-*m* is F_{15} -ZnTPP. This molecule was found to have an a_{1u} HOMO that contributes more heavily (50.9%) to the Q-state. The ET rate is an order of magnitude faster for ZnFbU-*m*, whose monomer analog ZnTPP has an a_{2u} HOMO that contributes 51.4% to the Q-state. Similarly positive correlations were observed for ET rates in the β -linked dimers.

One surprising finding is that the changes in contributions of the excited configurations to the Q- and B-states were relatively small. For example, the $(a_{1u})^1(e_g)^1$ contribution increased by only 2.3% from ZnTPP to F_{15} -ZnTPP. The large (order-of-magnitude) difference in ET rates for the analogous dimers suggests that the electronic communication is very sensitive to the details of the porphyrin excited states.

The quantification inherent in this approach allows us to correlate the configuration contribution with the ET rate, and to predict ET rates for unmeasured species. For example, F_5 -ZnTPP is the monomer analog for the F_{10} -ZnFbU-*m* dimer. Assuming a simple linear relationship between the square of the configuration contribution and the ET lifetime, F_{10} -ZnFbU-*m* should have a lifetime of 100 ps with Q-band excitation. Similarly, the predicted ET lifetime for F_{20} -ZnFbU-*m* was determined to be 160 ps. Similar analyses can be applied to the β -linked systems. This simple linear relationship is not likely to be generally appropriate, as it predicts lifetimes of below zero for $(a_{2u})^1(e_g)^1$ components of $>51.7\%$. However, since only two experimental points are available, it gives a reasonable starting point and predictions to which to compare future experiments and refine analyses.

The model also predicts that the ET rates should demonstrate wavelength dependence. First, there is a gross dependence upon the excited state in resonance with the exciting laser pulse. While the identity and contribution of the HOMO dominates the Q-band experiments, the rates measured from excitation in the B-band should be primarily influenced by the HOMO-1 orbital. A second type of wavelength dependence is more subtle, and arises from symmetry. Contrary to our assumption, the first two LUMOs in the porphyrins in dimers are not necessarily (i.e., by symmetry) degenerate. The *x*- and *y*-polarized transitions are therefore also not degenerate, and ET lifetimes should vary as the excitation source is tuned through the Q- or B-bands.

All of the calculations and correlations described thus far have relied upon high-level DFT calculations upon porphyrin monomers as analogs for dimer systems. We have also performed dimer calculations upon a limited subset of systems. Geometry optimizations under D_{2h} symmetry constraints were carried out at the B3LYP/6-31G(d,p) level for the ground states of the bis-ZnTPP dimers linked at the meso-positions (Zn_2 U-*m* and F_{30} - Zn_2 U-*m*). The results show that the HOMO is a_{2u} -like for Zn_2 U-*m* and the splitting between the a_{2u} -like and a_{1u} -like orbitals is 1.6 kcal/mol. As

with the monomers, the HOMO of the perfluorinated complex was found to be a_{1u} -like, with an a_{1u} – a_{2u} energy splitting of 0.9 kcal/mol. These results are very similar to those found for the ZnTPP (1.7 kcal/mol) and F₁₅–ZnTPP (0.9 kcal/mol) monomer analogs, respectively, and provide strong support for the soundness of our approach. Further dimer calculations are underway.

The orbital ordering and spacing of ZnTPP derivatives have been studied with high accuracy. We further quantify the relationship between frontier orbitals and the excited state configurations, and draw correlations to observed ET rates. The quantitative nature of the approach allows the model to be experimentally tested and refined. This approach may allow for the rational design of new porphyrin arrays with desired properties and photochemical responses.

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