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Electronic structure of tetra(4-aminophenyl)porphyrin studied by photoemission, UV–Vis spectroscopy and density functional theory

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A B S T R A C T

The valence and conduction bands of a thin film of tetra(4-aminophenyl)porphyrin (TAPP) are investigated by direct and inverse photoemission as well as by comparison to density functional theory (DFT) calculations. By projecting the electronic eigenfunctions onto the molecular framework it was possible to interpret the origin of each spectroscopic feature. Although the majority of the photoemission spectrum is attributed to the unsubstituted tetraphenylporphyrin (TPP) parent molecule, several features are clearly due to the amino substitution. Substitution also has important consequences for the energy positions of the frontier orbitals and therefore on the low-energy electronic excitations. The measured electronic transport energy gap ($E_g = 1.85$ eV) between the highest occupied molecular orbital (HOMO) and lowest unoccupied (LUMO) in TAPP is found to be significantly reduced with respect to TPP. Moreover, an increased energy separation between the two highest occupied states (HOMO and HOMO–1) is found both experimentally and by DFT calculations. Such evidence is attributed to an increased HOMO orbital destabilization due to an enhanced electron-donor character of the phenyl substituents upon amino functionalization. Finally, the above findings together with further time-dependent DFT calculations are used to interpret the effect of the amino groups on the UV–Vis absorption spectrum, namely an overall red-shift of the spectrum and remarkable intensity changes within the Q band.

Keywords:

Substituted tetra-phenyl porphyrins
Photoemission
DFT
UV-Vis spectroscopy

1. Introduction

Porphyrins are a widely studied class of chromophores playing a crucial role in several biological phenomena. The π -conjugated electron system of the central macrocycle is at the origin of many of the photo-chemical properties of porphyrins such as light harvesting [1,2], cancer photo-dynamic therapy [3], molecular oxygen transport [4], etc. Engineering of the opto-electronic properties of porphyrins thus continues to stimulate an intense research activity. Important modification to the porphyrin spectral response can be obtained for instance by functionalization [5,6], nano-structuration of extended porphyrin-based architectures [7,8] or adsorption on a substrate [9–11].

The optical spectra of porphyrins and porphyrin-based materials depend crucially on their frontier molecular orbitals (MOs) [12–14]. This is well known since the cyclic polyene [15] and Gouterman four-orbital [12,13] models which have been subsequently supported by several ab initio studies (see for instance [16] and references therein). The possibility of modifying the energy of such orbitals by substitution of the porphyrin ring has stimulated a great deal of work in recent years. For instance, it has been shown that adding functional groups to the porphyrin macrocycle at the methine bridges linking together the four pyrrole rings (that is *meso*-substitution) produces an overall red shift of the optical absorption spectrum associated with a reduction of the HOMO–LUMO gap [17]. Moreover, substitution causes a hyperconjugative delocalization of porphyrin π states that splits the quasi-degeneracy of the HOMO orbitals [18]. Eventually this has important consequences on the wavelength and intensity of the B (Soret) and Q bands, e.g. the Q bands can be enhanced by lifting the degeneracy of the HOMO orbitals [14]. Tetra-phenyl substitu-

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tion is intensely studied in this regard as it is commonly performed and has a strong influence on the optical spectra [17,19]. Several theoretical and experimental studies were performed on tetraphenyl porphyrin (TPP) leading to a consistent understanding of the related opto-electronic structure [12,17,16,19,20]. A natural development consists of substituting the TPP phenyls with functional groups capable of tuning the opto-electronic properties [21,22]. Very recently peripheral functionalization was also studied to develop nano-structuration properties [23–25] including the formation of covalent organic networks [26–28].

By studying in detail the filled and empty MOs as well as the optically excited states of tetra(4-aminophenyl)porphyrin (TAPP), the present paper aims to outline the modifications induced by adding electron-donor amino groups at the benzene *para*-position of TPP. By paying special attention to the modification of the electronic transport gap (E_g) and the binding energy (BE) of the four frontier MOs, it is shown that photoemission combined with (density functional theory) DFT calculations can be a powerful tool to predict the optical properties of individual molecules.

The first part of the paper reports on direct and inverse photoemission taken on thin films of TAPP. By comparing the spectra to previous studies it was found that: (i) the electronic transport gap is 1.85 eV, smaller than that for TPP [29]; (ii) several spectroscopic features not present in the TPP spectrum are detected in the occupied states whereas the unoccupied states are almost unchanged. Density functional theory (DFT) calculations using the B3LYP exchange correlation functional were performed on both TAPP and TPP. The comparison shows that the spectral differences originate from MO having important contribution from the amino groups and substituted phenyls. Moreover, a clear change upon substitution was found in the energy separation of the low-lying macrocycle-related HOMO and HOMO–1. Such evidence is corroborated by the present photoemission data. Finally the evolution found in the electronic structure upon substitution is used to interpret the changes in the UV–Vis spectrum of TAPP in solution through the four-orbital model. The interpretation is supported by time-dependent TD-DFT calculations of the low-energy singlet excited states.

2. Experimental and computational details

2.1. Experiment

Valence band ultra-violet photoelectron spectroscopy (UPS) and conduction band inverse photoelectron spectroscopy (IPES) experiments were performed in two different ultra-high vacuum (UHV) experimental apparatus. For UPS the substrate was the Au(111) surface, prepared by repeated cycles of standard sputtering (Ar^+ of 0.8 keV kinetic energy) and annealing (725 K). Commercially available TAPP molecules (5,10,15,20-tetrakis(4-aminophenyl)porphyrin (CAS 22112-84-1, Tokyo Chemical Industry) were first vacuum-sublimated on a glass tube to improve purity. The resulting deposit was scraped off and subsequently sublimated in UHV from a Mo crucible heated at about 675 K by a W filament. The deposition rate was about 1 ML per hour. Photoelectron spectroscopy measurements were performed at room temperature by an Omicron 125EA analyzer with standard Mg, $\text{K}\alpha$ and UV He I sources. X-ray photoelectron spectroscopy (XPS) was used in low resolution for checking molecular stoichiometry and for thickness calibration. UPS was performed with 5 eV pass energy and narrow analyzer slits resulting in 100 meV energy resolution. UPS spectra were taken at 45° emission angle. The energy scale was referenced to the Fermi level of the metal sample holder. The sample vacuum level was deduced from the secondary emission low energy cut off after polarizing negatively the sample. For the inverse photoemission experiment the TAPP molecules were UHV

sublimated from an alumina crucible. The substrate was a double-layer graphene grown by thermal annealing of a 3×3 reconstructed SiC(0001) surface. During evaporation the sample surface was kept very close (few cm) to the molecular evaporator allowing for a lower evaporation temperature (about 520 K) and higher deposition rate (about 1 ML/min). Normal incidence IPES spectra were performed in the so-called isochromat mode, that is by detecting photons of fixed energy (9.7 eV in the present case) through a band-pass detector while scanning the incident electron kinetic energy [30,31]. The process can be schematized as follows: when the impinging electron enter the sample by coupling with a surface or bulk state, it can drop to a lower unoccupied state with the emission of a photon. Higher photon counts are obtained for higher density of final states and the empty states spectrum is thus obtained by scanning the incident electron energy. A low electron flux (electron gun current of about $1 \mu\text{A}$) was employed so to minimize sample damage. The Fermi level was measured on the sample holder while the vacuum level was inferred from a target current spectroscopy measurement after having polarized the sample negatively. The UV–Vis absorption spectrum was recorded from a solution of TAPP in dichloromethane by a UV-2600 Shimadzu spectrometer.

2.2. Computational details

All TAPP structures were fully optimized using conjugate gradient methods with the GAUSSIAN03 [32] software package. The B3LYP hybrid functional [33,34] was used. The geometry optimizations were done with the B3LYP/6-31G* scheme and the stationary points were characterized as minima by a vibrational analysis. The energy was calculated using the 6-311+G* basis set (single point calculation). The optimization step was followed by a Mulliken population analysis in order to obtain the charge and spin density on each atom. In the optimized geometry, the amino-phenyl groups are tilted by 63° with respect to the macrocycle plane, in fair agreement with what found previously for the TPP molecule (67°) [35]. Subsequently the ground state geometries were employed in the excited state calculations using the spin unrestricted time-dependent DFT method [36–38]. The excitation energies, calculated using the B3LYP functional and the 6-311+G* basis set, thus correspond to vertical transitions.

3. Results and discussion

UPS and IPES are preferred tools to monitor the evolution of the frontier orbitals of π -conjugated organic molecules [39]. In fact, several studies have proven that the spectral features measured on thin films¹ are equivalent to those measured on better resolved gas phase spectra [18,20,40–42] and can then be compared to calculated density of states (DOS). In Fig. 1 the UPS and IPES spectra of a thick film of TAPP deposited, respectively, on Au(111) and graphene are compared with the B3LYP/6-311+G* DOS calculations of TAPP and TPP obtained by Gaussian convolution (0.2 eV FWHM) of the Kohn–Sham (KS) eigenvalues of the ground state configuration (vertical bars at the bottom). The film thickness is approximately 5 ML, thick enough to rule out any interaction of the probed molecules with the substrate. This is supported by the absence of any substrate feature such as Au $5d$ states in the UPS [43] or the strong π^* feature of graphene in the IPES [31]. The bottom energy scale represents the BE of the UPS/IPES spectra referenced to the sample Fermi level, the top energy scale refers to the vacuum level. The same value of the vacuum level ($E_{vac} = 4.3$ eV) was found

¹ Organic molecules in thin films are known to interact among each other through weak van der Waals forces.

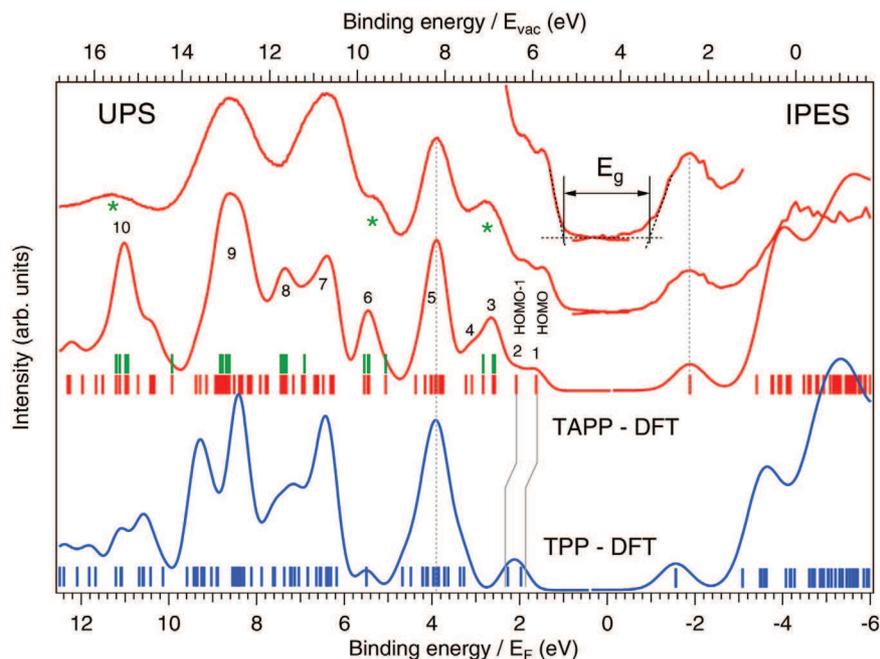


Fig. 1. TAPP UPS and IPES spectra (upper curves) compared with KS eigenvalues (filled and empty states) of TAPP (red) and TPP (blue). The calculated spectra are obtained by convolution of the eigenenergies (vertical bars) with a Gaussian function of 0.2 eV and 0.5 eV FWHM for the filled and empty states, respectively. The calculated spectra are shifted in energy to align the phenyl-derived peak to the experimental feature at about 3.9 eV. The TAPP eigenvalues having substantial contribution from the amino groups are displayed as green bars. The calculated spectral features of TAPP that mark a clear departure from the TPP spectrum are labeled with an asterisk. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

for the thick film of TAPP/Au(111) and TAPP/graphene, allowing the plotting of the UPS and IPES spectra of the TAPP on a common energy scale. Both the TAPP and TPP calculated occupied eigenenergies and spectra were shifted so as to align the BE of the peak at 3.9 eV to its experimental counterpart (dashed line).² A similar procedure was applied to the unoccupied states where the calculated values of TAPP are shifted so to align the LUMO to the experimental value. The same shift was applied to the calculated unoccupied states of TPP.³

Let us first compare the TAPP experimental and simulated spectra. A first inspection reveals that all the main spectroscopic features are remarkably well reproduced in energy and intensity. This confirms the capability of the B3LYP hybrid functional in treating satisfactorily electronic correlations of extended π -conjugated organic molecules due to the presence of a fractional exact exchange coupled with a non-local potential which reduces the self-interaction errors of semi-local approaches (see for instance Kronik et al. in [44]). Each of the eigenstates reported in Fig. 1 is a MO delocalized across the molecule. Among these, the HOMO and HOMO-1 states appear as isolated non-degenerate MO features at low BE. They are shown in Fig. 2 (as well as those of the nearly-degenerate LUMO and LUMO+1) and are similar to those found previously for the same system [22] and for the parent TPP molecule [16,17,19,20,45-47]. For the rest of the spectrum each spectroscopic feature (peak) results from several MOs and there is no simple trend to attribute its origin to specific atoms in the

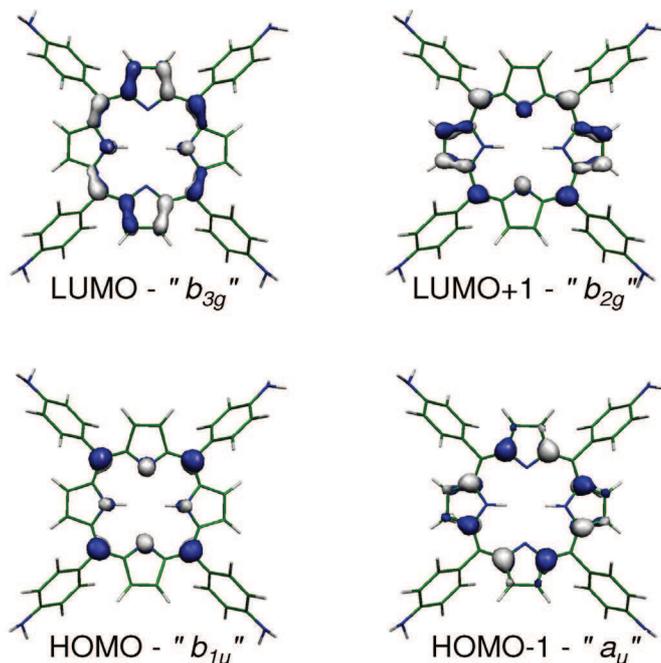


Fig. 2. The spatial distribution of the four TAPP's frontier MOs. Although the present calculations were made without symmetry restrictions the resulting MOs are very similar to those of the unsubstituted free-base porphine (see text). In order to ease the discussion the symmetry labels of the D_{2h} symmetry are then reported in quotes.

² Such procedure, also used in other studies [42] is necessary since the UPS spectrum was taken on a solid surface, a fact that is not taken into account in the calculations. The choice of the peak at 3.9 eV was made because this peak is very well defined and it is present in un-substituted TPP allowing the best overall agreement between experiment and calculation.

³ Such rude approximation does not affect the discussion on the amino contribution on the spectral shape. The modification of the energy gap upon substitution is made only through comparison of experimental data of the present paper with existing literature.

molecule. In the following an assignment is made by projecting the eigenfunctions corresponding to a given peak onto the molecular framework. The features of the calculated spectrum are numbered to facilitate the discussion and trends are given on the effect of the amino groups on the DOS. At binding energies higher than the HOMO-1, there is a peak at around 2-3 eV which is not found in the UPS spectrum of TPP [18,20,42]. Accordingly, the calculated coun-

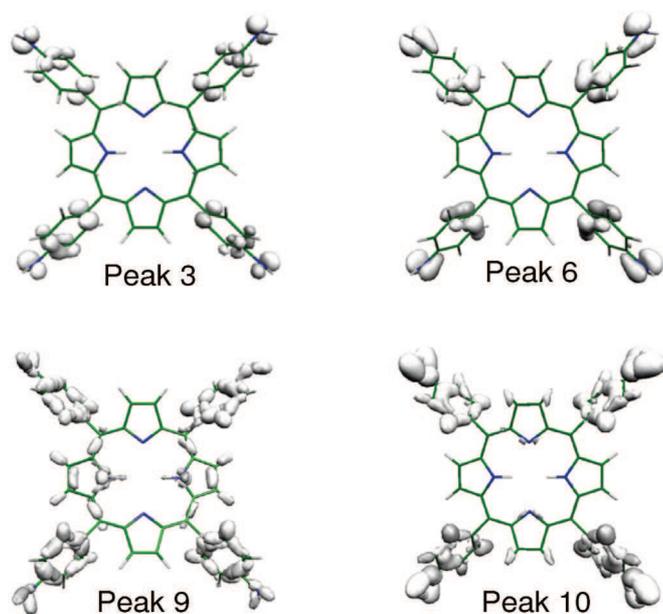


Fig. 3. Squared sums of several MO giving rise to well-defined spectroscopic features in the UPS spectrum. Labels refer to peaks in Fig. 1. Peaks 3–10 clearly originate from states localized on amino groups.

terpart, Peak 3, is absent in the calculated spectrum of TPP (blue curve in Fig. 1). The other features that display a clear departure from the TPP experimental [18,20,42] and calculated spectra are Peak 6 and Peak 10. These three peaks are marked with an asterisk in Fig. 1. To determine the contribution of the amino substituent to these features, the eigenenergies having significant contribution from these groups are reported in green as a separate set of vertical bars over the complete set of KS eigenvalues. As can be seen the three features mentioned above all originate from the amino groups. This can also be appreciated in Fig. 3 where the MO contributing to Peaks 3, 6, 9 and 10 are summed. As expected, the deeper lying orbitals (namely those contributing to Peaks 9 and 10) show a higher σ -character (higher inter-atomic orbital density). For the rest of the spectrum a very close similarity is found with previous data on TPP thin films [20] and gas phases experiments [18,41,42]. Specifically, Peak 5 has a strong contribution from the four phenyl groups (but not the amino groups) although in the case of TAPP an important spectral weight to Peak 5 is also found to come from the macrocycle. Feature 7 has contributions from the entire molecule. At higher BE, the amino substituent modifies sizably the feature around 8–9 eV: the two peaks observed for TPP in this energy range [42] merge into a single feature. The corresponding peak of the calculated spectrum (Peak 9) has a similar composition to that of Peak 5 except that the amino groups also have a significant weight (see also Fig. 3), particularly at the center of the feature.

The unoccupied part of the DOS was measured by IPES (right hand side of Fig. 1). Two intense features are visible in the spectrum. The first comprises the nearly-degenerate LUMOs centered at 1.9 eV above the Fermi level. The second feature is well separated from the LUMOs and results from the contribution from several MOs. For comparison the calculated unoccupied states of the TPP are also reported.⁴ As seen in Fig. 1 the overall shape of the empty states is not much affected by amino substitution.

⁴ The same binding energy shift as that used for TAPP was applied to the empty states of TPP.

Table 1

HOMO to LUMO E_g measured by direct and inverse photoemission as well as HOMO to HOMO–1 energy gap values from UPS and DFT. All values are in eV.

	E_g	HOMO–HOMO–1	
		UPS ($2B_{1u}-2A_u$)	B3LYP ($b_{1u}-a_u$)
TAPP	1.85	0.40	0.46
TPP	2.5 [54]	0.27 [18]	0.30

Although not rigorously appropriate for TPP and TAPP, the molecular symmetry of the MO and excited states refers, for simplicity, to D_{2h} free-base porphine.

Table 2

TD-DFT-calculated lowest singlets (in eV) for TAPP and TPP (taken from [19]). Values in parenthesis are the calculated oscillator strengths (normalized to the B band). The fourth column quotes the energy difference between the calculated B and Q band (see text for details).

	B	Q_y	Q_x	B–Q
TAPP	2.97 (1)	2.17 (0.11)	2.05 (0.06)	0.86
TPP	3.19 (1)	2.3 (0.09)	2.15 (0.01)	0.96

Measuring both the filled and empty states of a system gives access to its electronic transport energy gap (E_g) [48–50]. This is given by the energy separation between the leading edges at the HOMO and LUMO intersecting the zero-emission baseline (see Fig. 1). In the present case a band gap $E_g = 1.85 \pm 0.10$ eV is found for TAPP, a value that is substantially smaller than the value of $E_g = 2.5$ eV extrapolated for TPP from Ref. [29].

The analysis now focusses on the HOMO to HOMO–1 energy separation in the UPS spectrum. Comparing the available UPS data taken on TPP [18,20,42,51] with the present spectrum shows that a clear change is induced by amino substitution. As summarized in Table 1, for TPP in gas-phase the HOMO to HOMO–1 energy separation is reported to be 0.27 eV [18]. For TAPP a least squares fit (not shown) of the low energy region of the UPS spectrum was performed using Gaussian functions, giving a value of 0.40 ± 0.01 eV for the HOMO to HOMO–1 splitting.⁵ This trend is also present in the calculated spectra (Fig. 1 and last column of Table 1) and it is interesting to rationalize such BE changes upon substitution. In free-base porphine (H_2P) the two HOMOs are nearly degenerate and are assigned as b_{1u} and a_u (D_{2h} symmetry). In the UPS spectra of H_2P they correspond to $^2B_{1u}$ (HOMO) and 2A_u (HOMO–1) excited states, respectively [52], having an energy separation of 0.2 eV [53]. Using gas-phase PES and employing cross-section arguments Gruhn et al. [18] showed that substituting porphine with donor groups destabilizes the MO having a larger electron density on the substitution site. For instance, in free-base octaethyl-porphyrine (H_2OEP), anchoring octaethyl groups at the pyrrole sub-units destabilizes the a_u MO (notice the finite contribution for this MO at such sites in Fig. 2). Consequently, the A_u state ionization potential becomes smaller than that of the B_{1u} state. The HOMO peak is then the A_u state at 0.25 eV from the HOMO–1 B_{1u} peak [18]. For H_2TPP the order is inverted: the phenyls are substituted in *meso*-position at the methine bridges where the a_u MO has a nodal plane and the b_{1u} MO has strong electron density (see Fig. 2). The latter is destabilized by the charge-donating phenyls and is then the HOMO as in H_2P . In the UPS spectrum the corresponding B_{1u} peak is found at 0.27 eV (see Table 1) from the HOMO–1 A_u peak. In the present case of TAPP, since the aniline (the amino-terminated phenyl) is known to be an electron-donating functional group, the larger separation between the B_{1u} and A_u states observed by UPS and DFT indicates a further destabilization of the b_{1u} MO (see Table 1).

⁵ The uncertainty is mainly due to the background used to account for the secondary electrons.

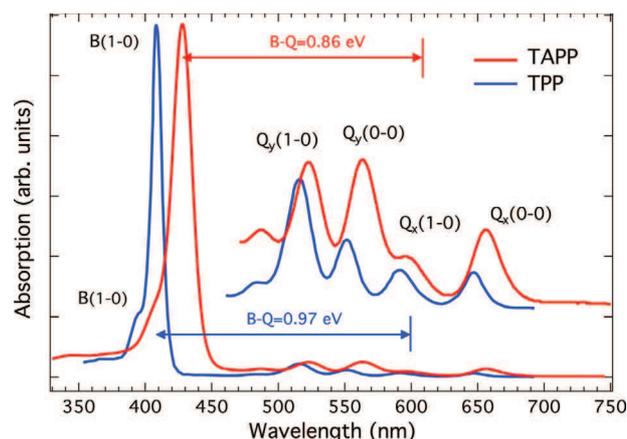


Fig. 4. UV-Vis spectra of TAPP (red curve) and TPP (blue curve taken from [55]) both in a dichloromethane solution. The intensity was normalized to the B maxima. The Q -band regions are multiplied by a factor 10 for better comparison. The measured $B-Q$ separations are to be compared with the calculated values in Table 2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

A redistribution of the frontier MO is known to have important consequences for the optical properties of substituted porphyrins [13,17,46,47,56]. In the following the evolution of the UV-Vis spectra of TPP upon amino substitution will be analyzed in the light of the UPS/IPES results and compared with TD-DFT calculations of the first singlet excitations (Table 2). The UV-Vis spectra of TAPP and TPP [55] are shown in Fig. 4. Both spectra show the typical spectrum of free-base porphyrin, namely an intense and narrow B (Soret) band separated in energy from the multi-peak structure of the much weaker Q band. Before analyzing the differences induced by the amino substitution, it is useful to recall the origin of the different features observed in these spectra.

Within the four-orbital model, the energy separation and relative intensity of the Q and B bands are explained in terms of mixing of excited-states [12,13]. The relevant optical transitions in this energy range are between the two highest lying MO (HOMO and HOMO-1) and the two degenerate LUMOs. When the HOMO and HOMO-1 are close in energy the excited states interact through configuration interaction thus splitting the absorption spectrum in two distinct bands (i.e. the B and the Q bands). Remarkably, within this picture the energy splitting between the B and Q bands increases for decreasing HOMO to HOMO-1 energy separation [12,13]. The striking intensity difference between the two bands is explained by symmetry arguments. The B band comes from symmetry-allowed high-energy transitions in which the relative phase of the mixing coefficients leads to the addition of parallel dipole moments. The mixing for the stabilized, low-lying excited states gives transition dipoles of opposite directions resulting in the weak Q band [14]. Interestingly the HOMO to HOMO-1 energy splitting also affects the absorption intensity: the closer these states are in the initial state the higher the B to Q intensity ratio [12,13]. At variance with metal-porphyrins, in free-base porphyrins the symmetry reduction causes the Q band to split in two sets of peaks: Q_x and Q_y having dipole transition moments aligned along the N-H bonds (H-H axis) and perpendicular to them respectively. Moreover each (0-0) transition is followed by a (1-0) vibronic replica due to coupling to several molecular modes, the most important being the stretching modes at methine bridges [57-59].

Returning to Fig. 4 the most striking effect is the red-shift of all features in the TAPP spectrum. UV-Vis spectra probe optical transitions within N-electron states whereas MOs measured by UPS/IPES correspond to $N-1$ and $N+1$ electron states which suffer of strong polarization effects in the solid state. This renders a

direct comparison between the values of the UV-Vis Soret band and E_g measured by photoemission inappropriate. Nevertheless, the red-shift in the absorption spectrum is successfully reproduced by TD-DFT (Table 2) and is in agreement to the reduced electron energy gap measured by UPS/IPES. The red-shift upon donor-*meso*-substitution was the subject of intense research in recent years. Studies have pointed out that a sizable in-plane nuclear reorganization is most likely the origin of the observed effect [17]. This hypothesis seems to hold in the present case where the presence of the amino groups is expected to increase the electron-donor character of the phenyls.

From a finer analysis of the UV-Vis spectra two other major differences can be observed. Namely, it is observed that i) there is a significant change of intensities within the Q -band: the $Q_{x,y}(1-0)$ peaks are almost unchanged while the $Q_{x,y}(0-0)$ have doubled their intensity; ii) there is a reduction of the $Q-B$ energy separation. This is evaluated as the distance between the B band (considered as a single feature) and the half-way point between the $Q_x(0-0)$ and $Q_y(0-0)$ bands [12]. This value is 0.97 eV for TPP compared to 0.86 eV for TAPP. Both aspects are remarkably well reproduced by TD-DFT calculations (Table 2) and can be understood on the basis of the four-orbital model sketched above and the present UPS/IPES/DFT analysis of TAPP. In fact, photoemission and DFT have revealed (Fig. 1) that amino substitution causes an increase of the HOMO to HOMO-1 energy separation together with an unchanged (within the present energy resolution) LUMO degeneracy leading to the enhancement of the Q band with respect to the B band as well as a reduction of the energy separation between the two bands. The fact that the $Q_{xy}(1-0)$ replica remain practically unchanged is not surprising since such replica are known to “borrow” intensity from the B -band [57,60] and their intensity vary little upon substitution [60].

4. Conclusions

The electronic properties of TAPP were studied by valence band UPS, conduction band IPES and DFT calculations. The comparison between calculations and experiment is very satisfactory. The assignment of the photoemission spectroscopic features to different parts of the molecules was performed and compared to theoretical spectrum of TPP. Electron-donor amino functionalization was found to reduce the HOMO-LUMO electronic transport gap and to increase the HOMO to HOMO-1 energy separation in a way that is consistent with an orbital destabilization process. These findings together with TD-DFT calculations were used to study the changes upon amino substitution of the UV-Vis spectrum. The present results strongly suggest that photoemission can become a complementary tool to address the molecular optical properties. Finally, because the binding energy of the frontier orbitals is known to change with molecular conformation [25], combining UPS and DFT will serve in the future – together with STM and X-ray absorption spectroscopy – to track conformational changes due, for instance, to molecule-substrate interaction.

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