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Electronic and Optical Properties of Magnesium Phthalocyanine (MgPc) Solid Films Studied by Soft X-Ray Excited Optical Luminescence and X-Ray Absorption Spectroscopies

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Abstract: In a study to link the optical and structural properties of solid films of magnesium Phthalocyanine (MgPc), a range of synchrotron based spectroscopic methods have been used. These include X-ray excited optical luminescence (XEOL) together with X-ray absorption spectroscopy (XAS) measured both by total electron yield methods (TEY) and by using the optically detected photoluminescence yield method (PLY). XEOL spectra below *K* shell threshold show a broad emission peak at ~860 nm which can be attributed to the optical Q-band of these organic systems, which is then suppressed above the threshold. The shift to higher wavelength compared to optical emission spectra from MgPc in solution is consistent with intermolecular coupling of the excited states in the loosely intermolecular bonded phthalocyanine crystal structure. Zero order total PLY spectra at both C and N *K* edges are compared to TEY spectra where at the C *K* edge an inversion of intensity ratios between features is observed. Wavelength-specific PLY absorption spectra taken at 860 nm at the N *K* edge show a role for σ^* states participating in the luminescence process possibly through the σ -like lone pair of bridging nitrogen atom, denoted the $n \rightarrow \pi^*$ transition.

Introduction

The use of small organic molecules and organic polymers in the fabrication of organic light emitting devices (OLED's) has generated considerable interest in the electroluminescence and photoluminescence properties of these materials and their films. Of particular interest is the interplay between optical properties, electronic structure, and morphology of OLED materials.¹ A typical OLED comprises a sandwich of an electron transport layer and a hole transport layer (both organic molecule/polymer) between two electrodes. Further, organic thin films can be used to tune the properties of electronic devices such as Schottky diodes,² and thin films of epitaxially grown hybrid organic–inorganic devices are being widely studied.

One of the foremost classes of planar organic molecular semiconductors, used in many organic optoelectronic devices principally as electron or hole transport layer, is that of the

family of metal phthalocyanines (M-Pc).³ Optical properties of these materials, among them the luminescence, are strongly related to the valence band electronic configuration and the excitation de-excitation process between highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO). There is quite extensive literature on the determination of the optical electronic transitions of these materials based on optical absorption and magnetic circular dichroism (MCD) spectroscopy mainly in the monomeric form of vapor phase and in solutions using various solvents.^{4–10} Traditional methods for increasing spectral resolution by measuring data from crystals or thin films at cryogenic temperatures fail because strong intermolecular interactions result in exciton coupling. The spectra of solid-state species as in thin

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films are extremely broad and very poorly resolved compared with data recorded from solutions.⁷

Interpretation of these spectra has been aided by theoretical analysis from calculated electronic configurations. Early calculations made use of semiempirical methods that are of questionable accuracy. The simple model of Gouterman and co-workers^{11–13} has been widely used and provides a reasonable description of the experimental spectra of main group porphyrin and phthalocyanine complexes. The model employs a four-orbital linear combination of atomic orbitals LCAO-MO (Hückel) with a theoretical treatment that unites a 16-atom, 18- π -electron cyclic polyene model to take into account the structure of the porphyrin ring.⁴ The main optical transitions of this model are usually referred to as the Q and B (Soret) transitions. Recently, density functional theory (DFT) methods were used by Liao et al. in a systematic study of a series of first row transition-metal phthalocyanines (M-Pc) that included MgPc.¹⁴ This calculation of their electronic structure has resolved doubts on the determination of some M-Pc ground states and has resulted in accurate calculations of their band gaps. Liao and Scheiner found differing molecular point group symmetries in the neutral and radical forms (D_{4h} and D_{2h} , respectively), which can result in the better determination of optical transitions and spectra for the free molecule. The rapid introduction of these materials as thin layers in OLEDs brought the need for further investigation of the optical transitions in the crystalline form. Works of Hollebone¹⁵ and Sharp¹⁶ gave the first absorption and MCD spectra of CH₂Pc, CoPc, NiPc, CuPc, and H₂Pc in crystal form and band shape analysis based on Davydov splitting in both the Q and B bands have given rise to good agreement with these observed spectra.

A recently developed synchrotron-based spectroscopy, X-ray Excited Optical Luminescence (XEOL),¹⁷ is employed here to explore the optical transitions in films of MgPc and assign them to luminescence centers. Furthermore, through Optically Detected X-ray Absorption Spectroscopy (OD-XAS), it is possible to relate luminescence to particular core sites, though this remains a challenge in such delocalized electronic system.

XAS involves the absorption of an X-ray photon to excited or ionized states resulting in emission of photoelectrons, Auger electrons and further secondary electrons, typically detected by total electron yield (TEY) methods. The decay of these core-hole excited states may through interactions of the Auger or secondary electrons with the valence states may result in energy being transferred to luminescent centers or chromophores through inelastic or shakeup processes. Thus, this can result in the creation of holes in valence band and electrons in conduction band for example in semiconductors, or in the occupied and unoccupied molecular orbitals (MO) of organic molecular semiconductors. In OD-XAS, the radiative recombination of these holes and electrons is measured. In XEOL, the spectral distribution of these photons is measured, and both can be a

probe of the core electronic structure that is related to luminescence.

Experimental Set Up

Measurements took place at the 6.1 Phoenix beamline station at the Daresbury Synchrotron Radiation Source using a combination of the MoLES apparatus¹⁸ and the ARUPS10 end station. This allowed the in situ study of epitaxial thick films (~ 900 nm) of MgPc grown on clean GaAs(001) in a growth chamber attached to the ARUPS10 end station which had a base pressure of $\sim 1 \times 10^{-8}$ mbar. It should be noted that all X-ray absorption, optical, and photoelectron spectroscopy measurements were obtained in situ in vacuum in the ARUPS10 endstation, where the base pressure was $\sim 9 \times 10^{-10}$ mbar, after sample transfer from the growth chamber. The GaAs(001) surface, with substrate dimensions of 7×7 mm, was prepared by sputtering and annealing and checked for contamination by photoemission and LEED until a clean well-prepared surface was available.¹⁹ The Knudsen cell used to evaporate the MgPc was thoroughly outgassed for several hours prior to deposition at a temperature just below the deposition temperature of ~ 360 °C, during which the pressure in the growth chamber was $\sim 1 \times 10^{-7}$ mbar. The rate of deposition was monitored before, during, and after by a quartz crystal thickness monitor where after the initial 5 monolayers were created a deposition rate of ~ 2 nm/min was used to create a film with a thickness of ~ 900 nm. Subsequently ex situ measurements of the thickness by spectroscopic ellipsometry were carried out, confirming a thickness of $\sim 906 \pm 62$ nm. The first and later stages of growth were confirmed by comparison of valence band photoemission of MgPc and X-ray absorption spectra. X-ray absorption near-edge structure (XANES) spectra at the C and N K edges of MgPc presented here were recorded in total electron yield (TEY) and by photoluminescence yield (PLY), with estimated monochromator resolutions of 0.17 at 280 eV and 0.24 at 400 eV. The TEY was recorded by the drain current method, while PLY was obtained in a total optical yield (zero order) mode, integrating over the optical response of the photomultipliers and then also at a selected wavelength or emission band. The luminescence was recorded at 90° to the incoming X-rays which had a grazing angle of incidence to the substrate surface of $\sim 30^\circ$ to facilitate the collection of the luminescence of the films by the attached MOLES apparatus. Apart from some of the collecting optics consisting of a lens, this was situated outside the vacuum but attached to the chamber. For the OD-XAS and XEOL measurements Hamamatsu R2949 and R758P photomultiplier tubes have been used with optical ranges of 185–900 nm and 160–930 nm respectively. Optical emission spectra were recorded using the low and medium energy gratings of a Jobin-Yvon optical spectrograph that is installed on MoLES with a nominal optical resolution ~ 6 nm and a spectral range spanning the visible/NIR between 400–930 nm. Samples were cooled down to liquid N₂ temperatures with an open cycle cryostat.

Results and Discussion

XEOL. X-ray excited optical luminescence spectra of MgPc have been taken at several excitation energies below and above thresholds of C and N K edges. Luminescence is obtained in

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the visible/NIR range (400–930 nm) at ~ 100 K and results in one significant broad optical emission at 860 nm which is most prominent for excitations below C *K* edge threshold (280 eV). This is ascribed to the Q-band in MgPc, normally the strongest emission feature. Above the C *K* edge threshold, the emission is substantially suppressed. At the N *K* edge a broad, weak signal has been obtained in the same range around 860 nm at excitation energies below threshold, but similarly the optical emission is further suppressed at excitations above the threshold. This suppression of intensity relates to the luminescent yield from these core levels as well as the attenuation length for the incoming X-rays within the film and is discussed later. Previous optical absorption measurements of MgPc in solution place the Q-band transition from the HOMO a_{1u} to the degenerate (in D_{4h} point symmetry) $2e_g$ LUMO¹⁴ at ~ 670 nm (fluorescence at 683 nm²⁰) whereas the B, N, L, S bands mainly lie below 400 nm.⁷ This substantial difference between solution (monomer) and crystal (polymeric) form have been previously reported in measurements on CH₂Pc, CoPc, NiPc, CuPc, and H₂Pc^{15,16} and have been attributed to Davydov splitting in both the Q and the B (Soret) bands.¹⁵ Davydov splitting arises from molecular exciton coupling which occurs due to the excited-state resonance interaction in loosely bound molecular systems. Recent photoluminescence measurements from vacuum-deposited MgPc films have shown the Q-band to peak at ~ 1.45 eV or 855 nm at room temperature consistent with our own observations.²¹ The observed emission was ascribed to the two Davydov components of the first singlet exciton band corresponding to the Q absorption band. Thus, the luminescence from the Q-band is measured in our XEOL spectra. When the transition dipole appears on the molecule upon excitation, the resonance interaction arises due to transition dipoles in translationally equivalent or inequivalent molecules.²² The molecular point group symmetry, for example, D_{4h} , is lowered from consideration of the unit cell, the space group symmetry, and the positioning of the neighboring molecules in the cell. Furthermore, intermolecular cohesive forces in the crystal may result in distortion of the molecule from the planar free-space form, with a consequent reduction in the molecular point group symmetry, all of which has an effect on the dipole moments of the molecule.^{23–25} This has long been established as having a significant effect on the optical spectra from organic molecular crystals.^{26,27}

Mizuguchi et al.²⁴ proposes a distorted molecule in the MgPc crystal with the Mg atom projected out of the plane of the four central nitrogen atoms by about 0.45 Å, forming a pyramidal structure that has been confirmed by Janczak et al.²³ The molecular symmetry is C_1 in contrast to D_{4h} usually assumed for MgPc in the free space; the excited-state of the metal phthalocyanine is doubly degenerate so the molecular distortion upon crystallization can remove the degeneracy to cause band splitting. Mizuguchi calculated that in the optimized geometry (D_{4h}) there is a degenerate absorption band at 711 nm whereas

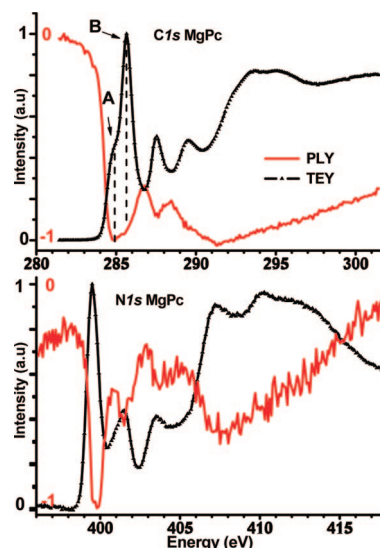


Figure 1. (Top) X-ray absorption spectra (XAS) of MgPc C *K*-edge in TEY and zero order PLY mode. (Bottom) XAS spectra at the N *K*-edge in TEY and in zero order PLY mode. In both cases, PLY spectra show inversion or a negative edge jump as compared to the TEY.

for the C_1 there are two bands at 712.9 and 699.5 nm; however, the splitting is too small to observe two distinguishable broad absorption bands in experiment. Moreover, he predicts an interplanar spacing along the *b*-axis of 3.19 Å which is considerably smaller compared with that of the other planar phthalocyanines. The distance between the Mg atom and the nitrogen atom in the upper layer is quite small and amounts to 2.70 Å. It is suggested that the Mg atom is in a position to accept an electron lone pair of the nitrogen atom from the upper molecule to form a five-coordinate complex in the solid state. As a result strong exciton coupling with spectra displacement and energy shifts may be expected. Calculations and absorption reflection suggested that the two bands should be around 625 and 829 nm. Similar measurements presented in Janczak et al.²⁵ are in agreement, showing two broad bands with the lower energy one being more intense. We only observed an emission peak at 860 nm, seen as an inset to Figure 2, which could be attributed to the calculated 829 nm band taking into account the Stokes shift. The photoluminescence spectra of Wojdyla et al.²¹ are in agreement with these measurements with a similarly large Stokes shift. A possible reason for not observing the first band is due to that fast vibronic modes may cause this excited-state relax radiationlessly and then decay through the lower energy transition.²⁸

OD-XAS. X-ray Absorption Near edge Structure (XANES) were recorded in total electron yield (TEY) mode and photoluminescence yield (PLY) at both C and N *K*-edges. These were measured at liquid N₂ temperatures. In Figure 1, the C and N *K* edge XAS spectra in TEY and zero order PLY are shown. The zero order PLY at both edges is inverted with respect to the TEY specifically showing a decrease in luminescence upon reaching the $1s \rightarrow \pi^*$ transition, but clearly reflects many of the same spectral features in both instances. This anticorrelation between the PLY and TEY is a well-known phenomenon in optical luminescence yield spectra²⁸ and has been thoroughly

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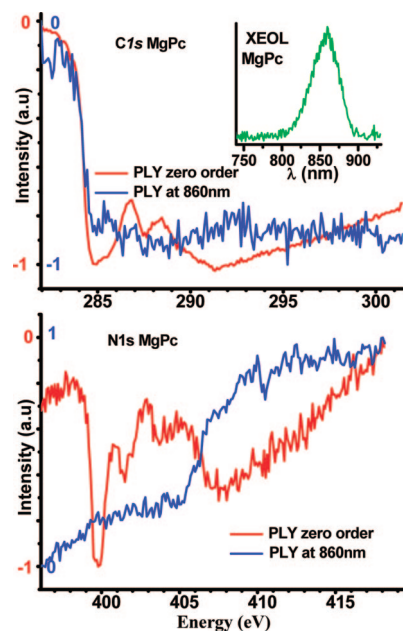


Figure 2. (Top) X-ray absorption spectra (XAS) of MgPc C K -edge at zero-order PLY and wavelength specific (860 nm) PLY. (Bottom) N K -edge at zero-order PLY and wavelength specific (860 nm) PLY. A positive jump on the partial PLY (860 nm) of N K -edge is attributed to a site (bridging nitrogen N_{bg}) and state ($n \rightarrow \pi^*$) selective luminescence channel. (Inset) X-ray excited optical luminescence (XEOL) spectrum of MgPc excited at 280 eV, below the C K -edge absorption threshold.

analyzed by Emura et al.^{29,30} Essentially, the negative edge jump seen in the PLY spectrum arises due to competition between different excitation-luminescence channels, each having different luminescence yields. In X-ray absorption below both the C and N K shell thresholds, all the shallow core levels of C, N, and Mg are excited and will participate in producing e–h pairs. Upon reaching the C K shell threshold, the $1s$ transition is turned on and the absorption cross section of C increases abruptly, particularly at the π^* resonance. As all elements and all accessible levels are competing for photons, if the luminescence yield for the C $1s$ excitation is less than from the shallower levels, then a reduction in the total luminescence PLY can be expected for a thick film. This is unlike the case of photoemission, which underlies the electron yield method where the electron escape depth is limited and the absorption channels do not compete. (Thinner films will still exhibit positive edge jumps because there is no longer the additional absorption from shallower levels deeper in the film.) This lower luminescence yield at the K edge may arise through a less effective coupling of the $1s$ core-hole excited-state to the luminescence chromosphere.

The $1s-\pi^*$ resonance of MgPc at the C K edge shows two prominent features which we denote as A and B, where the first is a shoulder of the main second peak as seen in TEY. These may be attributed to the $1s$ to π^* transitions of nonequivalent benzene (C–C) and pyrrole carbons (C–N) in the MgPc molecule where the aromatic carbons are less tightly bound with a lower C $1s$ binding energy.³¹ On that basis, it might be expected that the ratio A/B is the same ratio as C–C/

C–N, but this is not the case as the projected C $2p$ partial density of states on the pyrrole C site may be higher while the feature B may also consist of the ring C $1s$ to LUMO+1 transitions. Pyridine exhibits a similar anomalous ratio in the XAS spectrum³² where this is explained through inclusion of vibrational excitations leading to asymmetric line shapes with a tail on the high energy sides for each $1s-\pi^*$ excitation and this is also applicable to phthalocyanine systems.³³ It should be noted that in the zero order PLY this observed ratio is reversed from that observed in TEY wherein the A peak (C–C) is more efficient at reducing the luminescence than the B peak (C–N). Possibly, the pyrrole site (C–N) $1s-\pi^*$ excited-state couples more effectively to luminescence due to a faster transition of the electron to the chromosphere in comparison to the decay rate of the core hole than is the case for $1s-\pi^*$ excitation on the aromatic C site (C–C), may occur. The pyrrole C is bonded with the bridging N_{bg} where one of the chromospheres sites ($n \rightarrow \pi^*$)^{28,34,35} of the Q-band is located and the proximity with this neighboring site may enhance the coupling of the luminescence from this particular core level excitation in contrast to the C–C sites.

Another noticeable point is the loss of features in PLY after excitation around 288.5 eV, where the transition from C $1s$ to σ^* quasi bound states starts and the electron can tunnel out into the continuum. Luminescence resulting from the C $1s$ hole is further suppressed³⁶ because the participator Auger electrons are no longer involved in the decay of the core hole and the accompanied secondary processes leading to recombination of hole–electrons on the luminescence centers are absent. At the N K edge, the PLY shows the same inversion of the TEY with a monotonic increase of signal toward high energies consistent with observed increase of the luminescent quantum yield with higher excitation energies.³⁷

The inset in Figure 2 is the X-ray excited optical luminescence (XEOL), which is seen as a band centered at 860 nm, obtained with excitation energy just below the C K threshold. It is this band at 860 nm that is attributed to the Q-band transition. Wavelength specific photoluminescence yield (PLY) spectra were obtained at the C and N K edges with the optical spectrometer centered on this band, which is the strongest of the emission bands. Note that the zero-order PLY spectra include higher energy optical transitions such as the B (Soret) bands, which lie within the range of spectral response of the photomultiplier tubes as noted above. Thus the zero order PLY spectra include emission from the Q and B, and N, L, and S bands. Note that the optical emission can be confirmed as being from the organic film and not from the substrate from consideration of the attenuation lengths of the X-rays in the organic film, the ratios of the observed intensity of the XEOL before and after the C and N K edges, respectively (not shown),

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as well as the reversal of the ratio of features A and B in the OD-XAS at the C *K* edge.

Shown in Figure 2 are wavelength-specific PLY spectra obtained at 860 nm for both the C *K* and N *K* edges. The wavelength-specific PLY spectrum from the C *K* edge shows a negative edge jump at the threshold as the zero order PLY does but with no distinguishable features. This lack of features is indicative that there is more than one emission center and that the Q-band is not C *K* edge site related. On the other hand, interesting results emerge from the 860 nm wavelength partial PLY spectrum at the N *K* edge where a significant increase in luminescence is observed as the N $1s-\sigma^*$ range begins. Clearly, a site-specific and state-specific excitation channel that couples to the Q-band luminescence has been opened in this instance. This could be related to a σ -like molecular orbital derived from the 2p lone pair of the bridging nitrogen (N_{bg}).^{28,34,35} The $n \rightarrow \pi^*$ optical transition, previously assigned to N_{bg} sites has a significant vibronic coupling with the $\pi \rightarrow \pi^*$ optical transition from which the optical emission of the Q-band is derived.^{28,34,35} This should mean that the Q-band contains a substantial contribution of this ($n \rightarrow \pi^*$) band which is localized on the lone pair of N_{bg} . The difference in wavelength between these two optical transitions was ~ 70 nm (or ~ 0.2 eV),^{28,34,35} which is halved in ClAlPc where an electronegative axial ligand is present.²⁸ As Mizuguchi points out that the Mg atom in the MgPc crystal structure effectively becomes 5-fold coordinated, then this may be relevant to our case where this intermolecular Mg– N_{bg} interaction appears.

In conclusion, we have measured optically detected X-ray absorption spectra (OD-XAS) of thin films of MgPc, recording the zero order total photoluminescence yield at both the C and N *K* edges as well as the X-ray excited optical luminescence. The PLY at the C *K* edge shows a reversal of the intensities in the $1s-\pi^*$ structure in contrast to TEY. This may be accounted for by the pyrrole site (C–N) excited $1s-\pi^*$ excited-state coupling more effectively to luminescence due to a faster transition of the electron to the chromosphere than is the case for $1s-\pi^*$ excitation on the aromatic C site (C–C). Further, the partial photoluminescence yield obtained at 860 nm at the N *K* edge shows an increased coupling to luminescence once the $1s-\sigma^*$ threshold has been reached. Time-resolved XEOL studies may shed further light in the excitation dynamics and fluorescence properties of this and other metal phthalocyanines.³⁸

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