Coupling between Surface Plasmon Resonance and X-Ray Absorption in Co-Phthalocyanines/ Au bilayers (2)

Introduction

Metal-phthalocyanines (MPc) are macrocyclic planar aromatic molecules (Pc) in which a central metal atom (M) is bound to the organic structure. Interestingly, a large number of M substitutions are possible [1] in these molecules, giving rise to special electronic and optical [2,3] properties. In comparison with other organic semiconductors, MPcs have exceptional thermal and chemical stability. Therefore, they play an important role in nanotechnology through a wide range of applications such as field effect transistors [4], light emitting diodes [5], chemical sensors [6], biological photosensitizers [7], and photovoltaic devices [8]. Additionally, they are considered to be promising materials for the development of low-dimensional organic molecular magnets [9,10,11].

Most of the physical properties of transition metal substituted MPcs are related to the overlap between the 3d electronic states of the metal and the ligand 2p states of the Pc. This superposition of states gives rise to a combination of localized and delocalized states near the Fermi level [11]. Therefore, understanding these electronic configurations is of fundamental relevance to the development of MPc-based technologies.

Synchrotron X-ray-based techniques like soft X-ray photoelectron spectroscopy (SXPS), soft X-ray emission spectroscopy (SXE), X-ray energy spectroscopy (XES), and X-ray absorption spectroscopy (XAS) including both extended X-ray absorption fine structure (EXAFS) and near edge X-ray absorption fine structure spectroscopy (NEXAFS) allow the exploration of the electronic configuration of organic and inorganic compounds. These techniques are element and site sensitive providing precise information about the electronic transitions to bound vacant sites just above the Fermi level or chemical information like formal valence and coordination environment, and charge transfer mechanism with the substrate [9].

Although synchrotron X-ray techniques have been successfully used for the determination of the electronic states of the MPcs ([11] and references therein), the high X-ray intensity in combination with long exposure times (~10 to 60 min) frequently result in radiation damage. Examples of reported radiation damage on MPcs include SnPc, during SXPS measurements [12], CuPc thin films during SXE spectroscopy [13], and FePc during XES spectroscopy [14]. These reports provide clear evidence of radiation damage on MPcs and discuss possible effects on their electronic properties. However, a systematic study that correlates the impact of the observed radiation damage on the specific physical properties of MPc is still missing. Addressing this problem clearly requires the design of experiments that allow monitoring a specific physical property while the sample is under irradiation.

In this work, we use a state-of-the-art SPR instrument that is compatible with X-ray irradiation at a synchrotron beamline [15]. This set-up allows measuring *in situ* SPR in organic thin films subject to X-ray irradiation to determine the time dependence of the refractive index of CoPc thin film [16].

Our results show that X-ray irradiation effects are accumulative and partially reversible. By performing a scan in X-ray energy across the Co K-edge (7.724 keV) we determine that the observed radiation effect does not correlates with the Co absorption edge and therefore is due to the interaction of the X-rays with the organic part of the molecule rather than its Co central atom. No detectable effects are observed as a function of the CoPc film thickness and morphology.

Experimental

Simultaneous X-ray irradiation and SPR measurements were conducted at the branch A of the BM25 *SpLine* beamline at the ESRF The European Synchrotron in Grenoble, France using a state-of-the-art SPR instrument specifically designed for this type of experiments [15]. The instrument follows the Kretschmann-Rather configuration for SPR [17] and its sensitivity allows detecting relative variations in the SPR curve of the order of 10^{-3} -10^{-4}.

X-ray irradiation was performed in the range of 7.70 to 7.75 keV, i.e. across the Co K-edge absorption value (7.724 keV). At this edge, the Co absorption coefficient increases by 2 orders of magnitude. The incident flux on the sample was estimated to be ~10^{11} photons·s^{-1}·mm^{-2} considering the sample angle, slits used and beam focusing.

A total of 6 samples (see sample description in Table 1) with different CoPc thicknesses and growth temperatures were studied. Samples were grown on silica glass substrates (UQG Optics) with a refractive index n=1.457 (λ=633nm). Prior to deposition, the substrates were cleaned with soap, rinsed with deionized water, and dried with nitrogen. The Au/CoPc bilayers were grown in an Organic Molecular Beam Epitaxy system at a base pressure of 10^{-10} torr. First, an Au layer of 60 nm thickness was deposited by electron beam evaporation at a rate of 0.3 Å/sec with the substrates kept at room temperature (RT). Subsequently, two sets of CoPc thin films of 2 nm, 5 nm and 10 nm thicknesses were deposited on the Au layer by thermal evaporation at a rate of 0.4 Å/sec with the Au layer- substrate at RT and a 200°C respectively. The Au and CoPc thicknesses were controlled by a quartz crystal microbalance which was previously calibrated using X-ray reflectometry. During CoPc deposition a mask covering half of the sample was used. In this way samples present a free Au surface that was used as a reference during the experiment. The sample geometry is depicted in Figure 1.
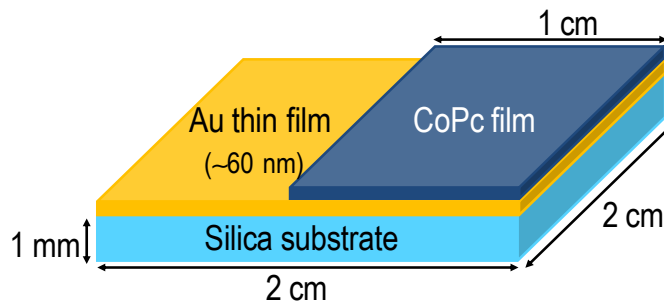

Figure 1. Configuration of the Au/CoPc samples studied in this work.

Table 1. Description of Au/CoPc samples with CoPc overlayer of 2, 5, and 10 nm nominal thicknesses grown at RT and 200 ºC on silica substrates.

Sample	CoPc thickness (nm)	Substrate Temperature (°C)
2-RT	2	20
5-RT	5	20
10-RT	10	20
2-200	2	200
5-200	5	200
10-200	10	200

The real and imaginary components of the dielectric constant of the CoPc and Au layers were obtained by fitting the experimental SPR data using the freeware software Winspall [18]. This code is based on the Fresnell equations for the system and includes the corrections for both reflection and refraction of the coupling prism.

The possibility of structural damage induced by X-ray irradiation was explored by means of micro-Raman spectroscopy, comparing spectra corresponding to irradiated and non-irradiated regions. Irradiated regions in the sample were identified with marks in the backside of the substrate for posterior study. Measurements were performed using a Witec Micro-Raman Confocal (Alpha 300R) system. Raman spectra were recorded in the spectral range of 0 - 3600 cm^{-1} with a Nd: YAG laser (λ=532nm) in p-polarization mode. The final spectrum is the result of an average of 40 spectra integrating 5 seconds each spectrum.

Results and discussion

We measured the effect of X-ray irradiation on all samples listed in Table 1 according to the following protocol: First, we align the laser and X-ray beams to coincide on the same area of the sample. Second, we record two SPR spectra before X-ray irradiation. By comparing these two spectra we determine the experimental error of our measurements. Third, we irradiated the sample with X-ray (7.72 keV) for 60 minutes. Then, with the sample still under irradiation, we recorded another SPR spectrum. Fourth, we switched off the X-rays, we wait 40 minutes and we take another SPR spectrum.

We have found that all the modifications of the SPR spectra due to X-ray irradiation reported here are at least one order of magnitude larger than the experimental error determined in the second step of the above mentioned protocol.

Figure 2a shows the SPR spectra for the sample 2-RT before, during, and after X-ray irradiation. Upon irradiation, the SPR curve increases its full width at half maximum value (FWHM) by 0.03°, the resonance angle shifts towards larger values ~0.01°, and the reflected intensity decreases 0.01 respect to the sample before irradiation. After 40 minutes without X-ray irradiation, i.e., during step 4, in the measurement protocol, neither the shift nor the broadening of the SPR spectra revert.
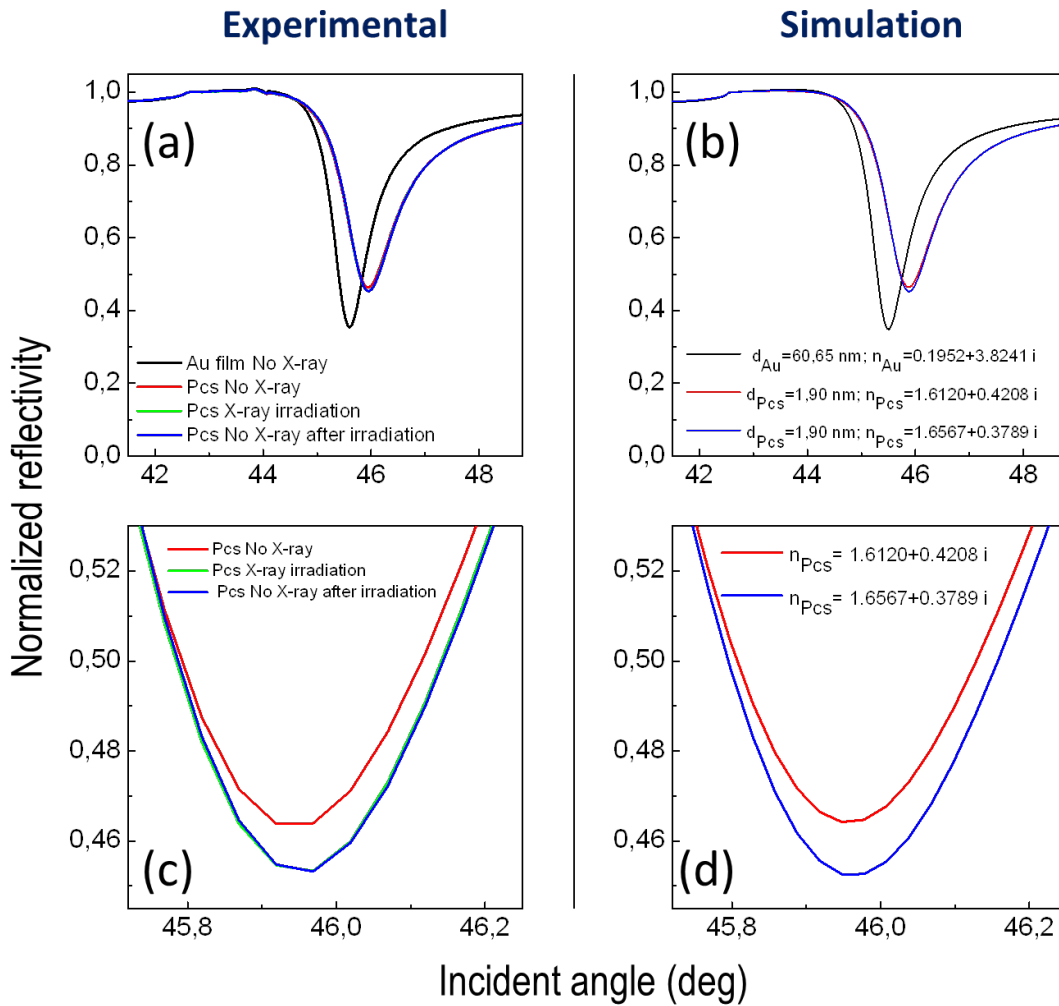
Figure 2. SPR curves for sample 2-RT. The black line represents the bare Au film of the sample. Red line corresponds to the CoPc film on Au region before, during (after 60 min irradiation with X- rays) blue line, and after 40 min without X-rays, green line. The irradiation was performed with 7.72 keV X-ray. (a,c) Experimental and (b,d) simulated curves. (c) and (d) show a detail of the resonance region. Spectra were normalized at the critical angle.

The SPR spectrum of Au/MPc bilayers is very sensitive to gas adsorption [16], the reason for their use as gas sensors [6,19]. Since synchrotron X-rays propagating in air produce ozone [20] and molecular cracking of N_2, CO or CO_2, the observed variations in SPR spectra could be ascribed to the absorption of ozone or C and/or N deposition on the CoPc film [21]. To rule out this possibility we carried out measurements of the reflectivity (at a fixed incident angle) versus time in an inert He atmosphere. The results of these tests show the same effects as in air, therefore we can

discard ozone or other atomic adsorption as the origin of the observed modifications. Consequently, we conclude that the observed variations in the SPR spectra are due to the interaction of the X-rays with the CoPc film.

To estimate quantitatively the magnitude of the SPR changes of the organic film upon irradiation, we simulated the SPR curves obtained before and during (after 60 min) X-ray irradiation that are presented in Figure 2. Since the quality of the Au thin film, particularly its thickness and roughness, may cause modifications in the SPR spectrum profile [22,23,24], we first fitted the SPR spectra corresponding to the bare Au region of the sample. For this fitting we considered a four-media system (prism/silica substrate/Au/air) with the refractive index of the glass substrate n_s=1.457 kept as a fixed parameter, and the Au film thickness, d_{Au}, and refractive index, n_{Au}, as free parameters. We have found that the best values of the refractive index and thickness for the Au film are d_{Au}=60.65 nm and n_{Au}=0.1952 + 3.8241 i. Subsequently, we fitted the SPR spectrum of the sample 2-RT prior to irradiation considering a five-media system (prism/silica glass/Au/CoPc/air). In this fit, we used the values obtained previously for Au (film thickness and refractive index) and the refractive index of the silica substrate, which were fixed parameters. The CoPc film thickness and refractive index were the only free parameters. We found the best fit for a CoPc thickness of d_{Pc}=1.90 nm and n_{Pc}=1.612 + 0.4208 i. We fitted then the SPR curves of the samples upon irradiation (after 60 min). For that, we assumed that the CoPc layer thickness remains constant during X-ray irradiation and that the refractive index is the only free parameter; attempts to fit the spectra leaving the thickness of the CoPc film as a free parameter resulted in meaningless fits. The best fit, n_{Pc}=1.6567 + 0.3789 i, indicates an increase of the order of 3% of the real part of the refractive index and a decrease of about 10% in the imaginary part.

To analyze the irradiation kinetics on the SPR properties of the organic thin films, we measured the reflectivity at a fixed incident angle of 45.95º [25]. Figure 3 shows the effects of 7.75 keV X-ray irradiation on the reflectivity, when switching on and off the X-rays. This result shows a decrease of the reflectivity upon irradiation and a partial recovery when the irradiation is interrupted. This effect is cumulative with X-rays dose.
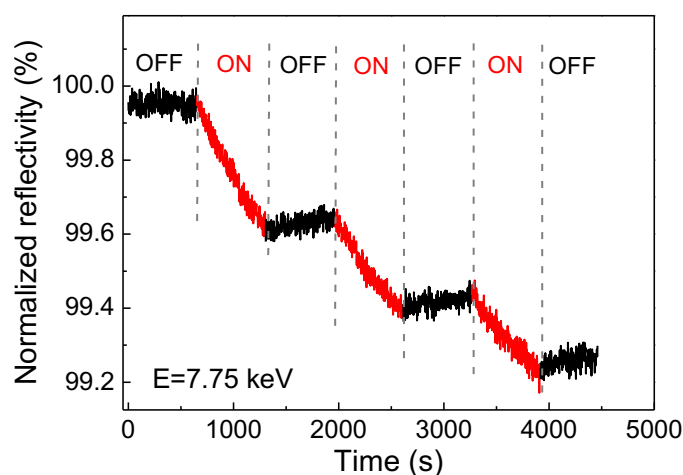
Figure 3. Reflected intensity (normalized to the initial value) versus time when switching on and off the X-rays at 7.72 keV, *in situ* and in real time for sample 2-RT.

To study the dependence of irradiation effect on the photon energy, and in particular on the X-ray absorption by the Co atom, we measured the reflectivity at a fixed incidence angle of 45.95º while scanning the X-ray energy from 7.70 to 7.75 keV. In Figure 4 we compare the XAS signal with the reflectivity of sample 2-RT. Although the XAS shows 2 orders of magnitude enhancement of the absorption coefficient from 7.705 keV, corresponding to the Co K-edge absorption, the reflectivity exhibits a monotonous decrease. This decrease is similar to the one observed in Figure 3 irradiating with a fixed energy. This implies that the radiation effect does not depend on the X-ray energy, at least within the explored 7.70 to 7.75 keV range pointing out that the irradiation effects originate mostly from the interaction of the X-rays with the organic part of the molecule and not the central Co atom.
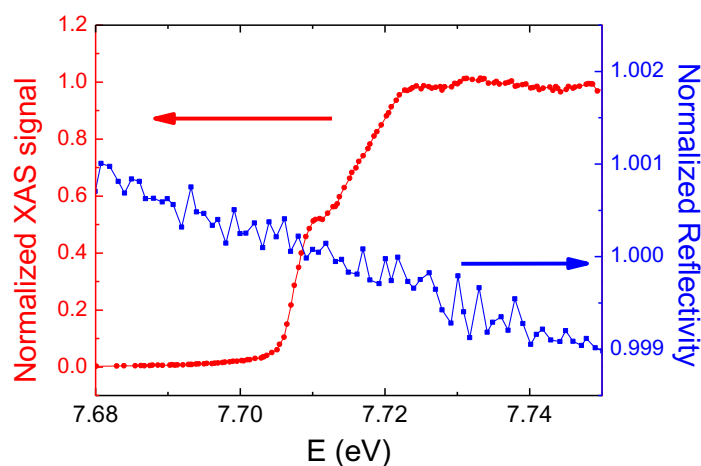

Figure 4. XAS spectrum for metallic Co (red circles) and reflected intensity of the laser beam versus photon energy (blue circles) measured simultaneously for sample 2 -RT.

The grain size and crystallographic phase of the MPc thin film depend on film thickness and growth conditions, like evaporation rate and substrate temperature [26,27]. In general MPc thin films grown at RT develop crystalline grains of 20 nm in average size while deposition at higher temperatures, e.g. 150°C, lead to more compact elongated crystallites with a larger size of ~50 nm [1,25]. Additionally, these morphologies exhibit different optical properties [28]. In order to explore the irradiation effect of X-ray as a function of CoPc thickness and morphology, we measure the SPR spectra upon irradiation on all of the samples listed in Table 1.

Figure 5 shows the experimental data and the analysis for sample 10-RT. The modifications of the SPR spectrum before and during irradiation are similar to those shown in Figure 2 for a thinner sample (2-RT). In general, the variations of SPR reflectivity and the FWHM are more pronounced for the samples grown at RT than those grown at 200 ºC. Moreover, the FWHM changes in the resonance for both organic films grown at RT and at 200 ºC, exhibiting larger modifications as the layer thickness increases. Resonance angle modifications do not show a clear tendency, neither with CoPc thickness, nor with grain size (growth temperature). The measured changes in the SPR parameters during irradiation for all the samples are summarized in Table 2.

Table 2. Modifications in the resonance region of SPR spectra of CoPcs on Au/silica after irradiation for 60 min at 7.72 keV. The +/- symbol represents SPR changes due to the irradiation towards larger/lower values with respect to the SPR spectrum of samples without irradiation.

Induced variations	2-RT	2-200	5-RT	5-200	10-RT	10-200
FWHM (deg.)	+ 0.03	+ 0.02	+ 0.06	+ 0.03	+ 0.08	+ 0.06
Shift of resonance angle (deg.)	+ 0.01	− 0.02	+ 0.03	− 0.04	+ 0.03	+ 0.03
Reflectivity at resonance (adim.)	+ 0.01	+ 0.006	+ 0.01	− 0.004	+ 0.03	+ 0.006

10 nm CoPcs grown at RT on a Au thin film

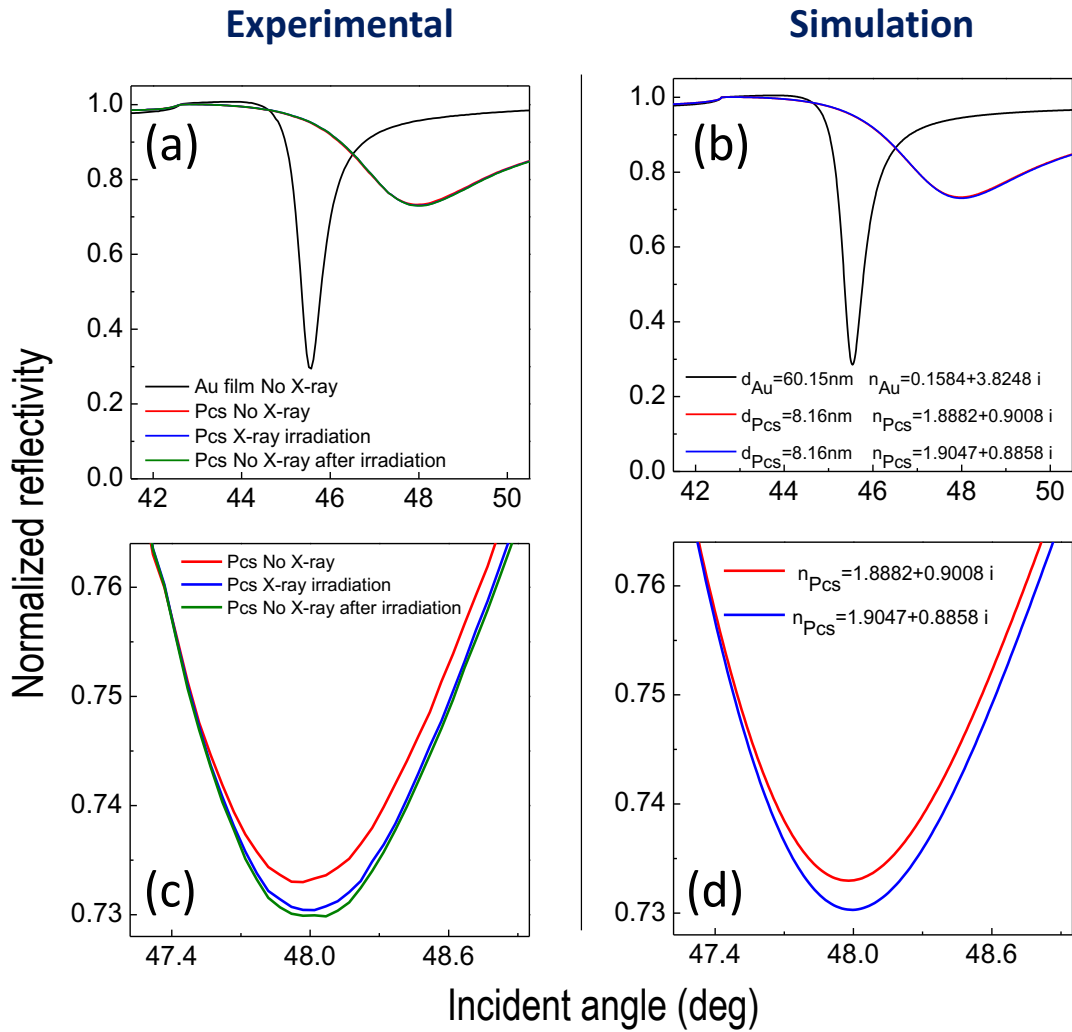### Experimental

Simulation

Figure 5. SPR curves for the bare Au film (black line) and for 10-RT before (red line), during (after 60 min with X- rays, blue line) and after (40 min without X-rays, green line) irradiation. X-ray energy is 7.72 keV. Figures (a) and (c) depict experimental data. Figures (b) and (d) show simulations. Figures (c) and (d) show a zoom-in around the resonance region. In all the cases the spectra were normalized at the critical angle.

We fitted the spectra of all the samples following the same fitting procedure described for sample 2-RT. This analysis shows non-systematic variations of the refractive index of CoPc films, between 0.3 % and 10 %, for samples with different thickness and growth temperature. The results of these analyses are summarized in Table 3.

In order to discard possible modifications induced in the Au film by the X-rays, we also fitted the spectra by fixing the thickness and refractive index of the organic film to the values prior to irradiation. In this way, we leave as free parameters those of the Au film. Under these assumptions, the refractive index of the Au needs to be changed about ~0.5% to account for the modification of the SPR spectrum upon X-ray irradiation. This 0.5% is 50 times larger than the upper limit of the possible changes for the bare Au films upon irradiation, which are of the order of 0.01% [29]. Thus, we conclude that the observed variations of the SPR spectra upon irradiation are associated only with modifications in the CoPc layers.

Table 3. Calculated thickness and refractive index variations of CoPc layers before and during (60 min) X-ray irradiation at 7.72 keV of CoPcs grown on Au/silica system.

	2-RT	2-200	5-RT	5-200	10-RT	10-200
CoPc thickness (nm)	1.9	2.1	4.5	4.9	8.2	8.8
n_{CoPc} **before X-ray irradiation**	1.6120+0.4208i	1.4903+0.4901i	0.5350+1.4853i	0.9240+1.6950i	1.8882+0.9008i	0.6518+1.7665i
n_{CoPc} **during X-ray irradiation**	1.6567+0.3789i	1.4575+0.4488i	0.4818+1.4803i	0.9712+1.7471i	1.9047+0.8858i	0.6259+1.7524i
Variation of real part (x100)	+2.8	-2.2	-9.9	+5.1	+0.9	-4.0
Variation of imaginary part (x100)	-10.0	--8.4	-0.3	+3.1	-1.7	-0.8

In order to determine if the modifications of the CoPc refractive index are due to permanent structural modifications induced by X-ray irradiation, samples were studied by micro-Raman spectroscopy. This technique can provide information about the crystalline order, size, and defects present on the organic thin films [30]. We analyzed all samples two weeks after synchrotron irradiation by comparing irradiated regions (at 7.72 keV for 60 min) with non-irradiated regions. In each case we measured four scans on the irradiated regions and two in the non-irradiated regions.
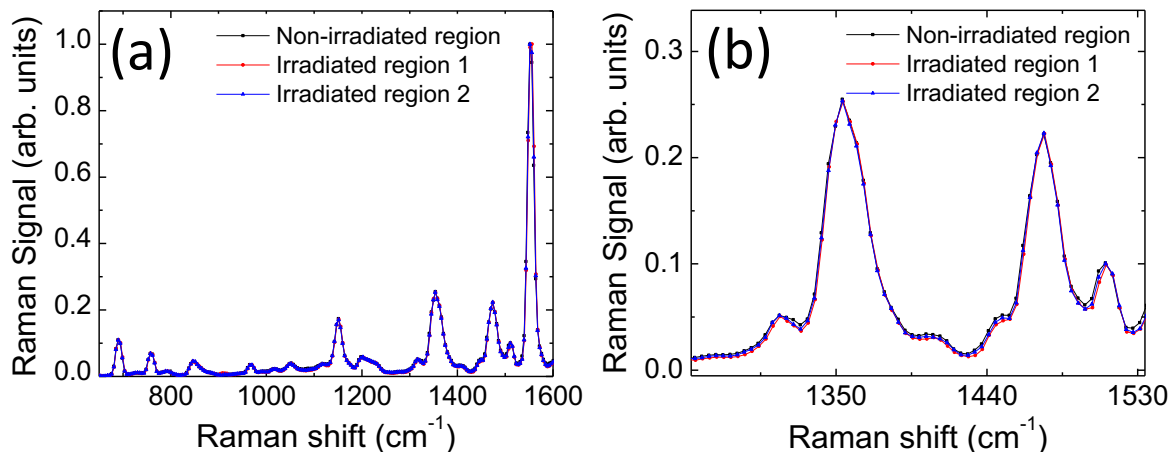
Figure 6. (a) Raman spectra on irradiated and non-irradiated regions for the sample 10-200 and (b) a detail of Raman spectra.

Figure 6a shows two Raman spectra from the irradiated region and one outside the irradiated region corresponding to sample 10-200. The bands in the spectra can be identified as corresponding to CoPc according to *Tackley et al.* and *Palys et al.* [31,32]. These results show no significant variations in the Raman spectra upon X-ray irradiation (see Figure 6a-b). Differences in band intensity and shifts between irradiated and pristine zones are of the same order as those found between two different irradiated regions and between non-irradiated regions. Similar results were observed for the rest of the samples. Consequently we conclude that there are no permanent structural modifications produced by the irradiation.

Since the change in SPR signal recovers partially after irradiation (see Figure 2), we performed a second experiment measuring the Raman spectra immediately (30 min) after irradiation with X-rays for 2 hours in a diffractometer (Cu K-alpha beam, 8.047 keV). This second experiment, confirmed the absence of measurable changes in the Raman spectra upon X-rays irradiation.

From this we conclude that observed variations upon irradiation originate in changes in the electronic configuration of the molecules. *Cook et al.* found that irradiation with soft X-rays of Pc films modifies the Fermi level [14]. Similar effects have been observed in semiconductors when introducing a very small number of gap states by dopants, deep traps, defects or interface states [33]. The refractive index of a material can be modified by changes in the lattice structure or through electronic modifications [34]. Thus, variations of the Fermi level between the HOMO and LUMO might induce modifications in the optical properties of a material [35]. According to *Cook et al.*, the more subtle radiation effect creates a small minority of defect states, which are

undetectable by structural probes but they are enough to vary the Fermi level position. This Fermi level shift increases with the irradiation time until saturation. While structural defects are more stable with time, changes in the electronic configuration recover faster with time as we observed in our experiments (see Figure 3). Therefore, it seems quite likely that the changes induced in the CoPc films by X-ray irradiation are related to changes in the electronic configuration than to structural modifications. Raman spectra and X-ray diffraction strongly support this hypothesis. The fact that the results are the same irradiating with X-ray energies below and above the Co K-edge imply that these modifications are related to the scattering of the X-rays by the soft matter and weakly related to the absorption of the Co atoms. Thus, similar effects can be expected for other type of phthalocyanines.

Conclusions

We have studied the effect of synchrotron X-ray irradiation around Co K-edge (7.724 keV) on CoPc thin films grown at RT and 200 ºC on Au film/silica substrate. Using SPR spectroscopy as a probe, we monitored the induced changes of the refractive index for CoPc layers by X-ray irradiation *in situ* and in real time. The modifications induced by the X-rays are cumulative and upon 1 hour irradiation with X-ray intensity of the order of 10^{11} photons $mm^{-2} \cdot s^{-1}$, reach between 0.3 and 10%, depending on layer thickness and growth temperature. After irradiation the effect is partially reversible. The effects of irradiation are very similar for photons with energy below or above the Co K-edge, suggesting that the damage mechanism is related to the scattering of X-rays in the organic portion and not to absorption by the Co atom. Consequently, a similar behavior may be expected for other types of Phthalocyanines. We could not find any structural change in the CoPc layer induced by X-ray irradiation, suggesting that changes of the refractive index are related to electronic modifications of the organic molecules and not to structural damage.

References

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