X-ray photoelectron spectroscopy of carbon in commercial copper phthalocyanine pigments

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Abstract

This paper presents systematic studies of the C1s signal in the X-ray photoelectron spectra of commercial Cu-phthalocyanine (CuPc) commonly used as a major commercial cyan pigment in a variety of printing applications. Although the CuPc pigment has been widely employed for many decades, the correct interpretation of the C1s signal in non-stoichiometric CuPc pigments has not yet been agreed upon. Our work demonstrates that the composite C1s CuPc signal consists of five components: two related to principal C positions within the CuPc macrocycle, two associated with shake-up transitions accompanying the principal C positions, and one due to mostly aliphatic impurities. A detailed analysis showed that magnitude of shake-up peaks was approximately equal 10% to 12% of their principal transitions, in agreement with theoretical calculations, while the impurities C1s signal corresponded to IR measurement of the aliphatic C-H vibrations. The proposed C1s interpretation has been successfully tested for a large number of commercial CuPc pigments and provides a guideline for routine XPS analysis of the CuPc that can provide a reliable pigment quality control.

Introduction

Copper phthalocyanine (CuPc) molecule form a planar structure consisting of a porphyrin-like ring surrounded by four peripheral benzene rings and a central Cu atom [1,2]. Though a number of potential applications of the CuPc in electronic devices have been proposed in the recent years [1,3,4], CuPc is primarily used as a major cyan pigment in variety of applications ranging from printing on a paper to fabric dyeing [2]. Thin film CuPc used for electronic applications is usually deposited by thermal evaporation, occasionally doped with atoms providing the desired electrical conductivity, and the ratio of its constituents is close to the CuPc stoichometric ratio. Mass-produced commercial CuPc cyan pigment used for printing frequently contains various 'contaminants', mostly organic additives providing desired ink properties. Concentration of the additives can be as high as several percent and the resulting mixture does not constitute stoichometric CuPc [2].

Photoelectron spectroscopy of the core CuPc electronic states employing the X-ray excitation (XPS: X-ray Photoelectron Spectroscopy) has been extensively used to characterize thin stoichiometric CuPc films [1,5,6]. However, only recently a consensus has been reached regarding the correct interpretation of the chemical shifts observed in the C1s composite XPS signal [5,6]. Although XPS can be also used to characterize pigment CuPc, there is no reported data demonstrating interpretation of the XPS spectrum of a nonstoichometric CuP pigment. This report presents a systematic XPS investigation of a series of commercial CuPc pigment samples and, in particular, the way of resolving the C1s signal into its constituents with the help of the corresponding IR absorption data.

Experimental

An extended series of commercial CuPc pigments were analyzed. They were obtained from different vendors in form of solid powders with average particle size of few hundred nm. For comparison, reference "raw" CuPc, acquired as a "chemical" (Sigma-Aldrich) rather than "pigment", was also analyzed. Highly conductive Si (100) was used as a substrate on which CuPc pigment samples were deposited. The Si substrates were cleaned following the normal IC cleaning process that included striping of the native oxide [7]. XPS specimens were prepared by depositing droplets of aqueous dispersion of a pigment and then allowing the water to dry out leaving behind a solid residual film. Alternatively, dry powder was pressed against a sticky, conductive tape mounted on the Si substrate until it formed a thick, continuous layer of powder. Identical XPS spectra were obtained for specimens of the same pigment prepared by both methods.

XPS measurements were conducted using a commercial XPS spectrometer equipped with a monochromated Al KαX-ray source (1486.6 eV) and the energy scale calibration was done using the adventitious C 1s signal (284.8 eV) due to residual hydrocarbons. The positions of the individual XPS peaks, their widths and amplitudes were determined by means of a non-linear least-square fitting of the experimental data with mixed Lorentzian-Gaussian functions (15:85 ratio)) and after the subtraction of the Shirley-type background. The quality of the fitting process was tested by simultaneously conducting the Pearson's χ^2 test; fitting was repeated until satisfactorily low value of the χ^2 was achieved. IR absorption was measured using a commercial research-grade FTIR spectrometer. IR spectra were obtained using pressed tablets containing CuPc pigment and optically neutral KBr providing transmittance between 10% and 90% throughout the entire measured IR spectrum.

Results and Discussion

According to recent reports [4-6] C1s spectrum of a high purity CuPc consists of two peaks corresponding to different carbon bonding configuration within the CuPc molecule, namely the carbon within a benzene ring (C1) and carbon in a pyrrole ring (C2). In addition, these peaks are accompanied by their shake-up satellite due to π - π^* transitions (SC1 and SC2). Their binding energies vary among the reports, but their respective values are approximately equal to 284.7 eV (C1), 286.1 eV (C2), 286.5 eV (SC1), and 288.1 eV (SC2). Deconvoluted C1s component peaks need to satisfy the following conditions: 1.) since the number of carbon atoms of benzene rings is three times more than the number of carbon atoms in pyrrole configuration within a CuPc molecule, the ratio of the XPS peak areas (C1+SC1) / (C2+SC2) should also be equal 3; 2.) the satellite peak area should be approximately equal 10% to 14% of the corresponding main peak area, in agreement with the calculated transition probabilities [6,8]. Both these conditions are satisfied by the high quality XPS results obtained for the thin film, vacuum evaporated CuPc.

Table 1. Atomic composition of measured CuPc samples (XPS) [a)].

#	C	N	Cu	O	Other impurities [b)]	C:N:Cu [c)]
1	76.8	15.8	3.2	3.6	0.6	24:4.9:1
2	76.4	16.7	3.0	3.3	0.6	25:5.6:1
3	76.0	15.7	3.1	4.5	0.7	24.5:5.1:1
4	76.8	18.0	3.3	1.7	0.2	23.3:5.5:1
5	75.2	4.3	0.4	13.7	6.4	188:10:8:1
6	75.3	17.0	3.5	3.6	0.6	21.5:4.9:1
7	76.5	17.8	3.5	2.1	0.1	21.9:5.1:1
8	69.3	13.1	2.2	11.5	3.9	31.5:6:1
9	78.7	15.1	2.4	3.4	0.4	32.8:6.3:1
10[d)]	74.4	18.4	4.0	2.8	0.4	18.6:4.6:1

[a)] atomic concentration as measured by XPS - presence of hydrogen is neglected; [b)] residual impurities found in some of the samples may include: S, Cl, Na and Si (originating from substrate); [c)] stoichiometric CuPc ratio = 32:8:1; [d)] reference sample (not pigment).

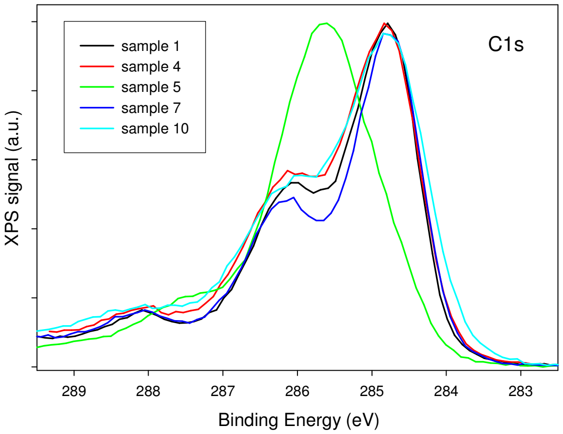

Figure 1. *C1s XPS spectra of CuPc samples - for clarity only few selected samples are shown.*

Table 1 presents the elemental composition of the measured pigments, while the corresponding C1s spectra of several selected pigments are shown in Figure 1. It is apparent that these spectra cannot be obtained by simply superposing the component peaks with the same set of binding energies for each pigment. For example, Figure 2 shows the best outcome of the fitting process (minimum χ^2 obtained) for a selected pigment using the aforementioned binding energies of a high purity CuPc. The result is a very poor fit; its χ^2 value is larger than 10. Similar results are obtained for other pigments. It is also apparent then even if a reasonable approximation of the XPS spectra for all pigments was obtained using the same set of binding energies for all pigments; the peak area ratios would not remain constant as in the case of thin, thermally deposited CuPc films.

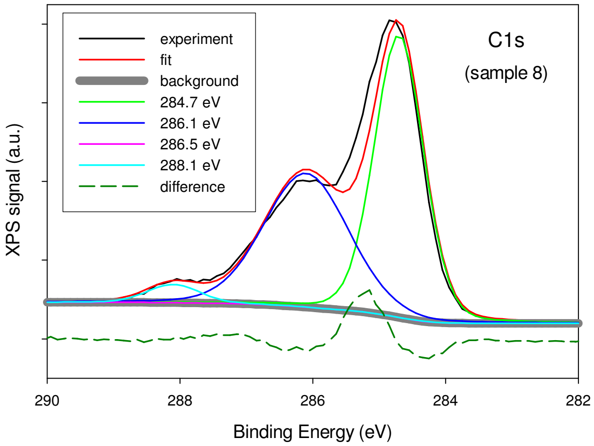

Figure 2. *The best four-peak fit obtained for sample 8 using the reported C1, C2, SC1, and SC2 values. FWHM were forced to remain below 1.5. The χ^2 value in this case was equal 19.5. Resultant C1/C2 was less than one and the difference (dotted line) between the experiment and fit showed unacceptably large variations.*

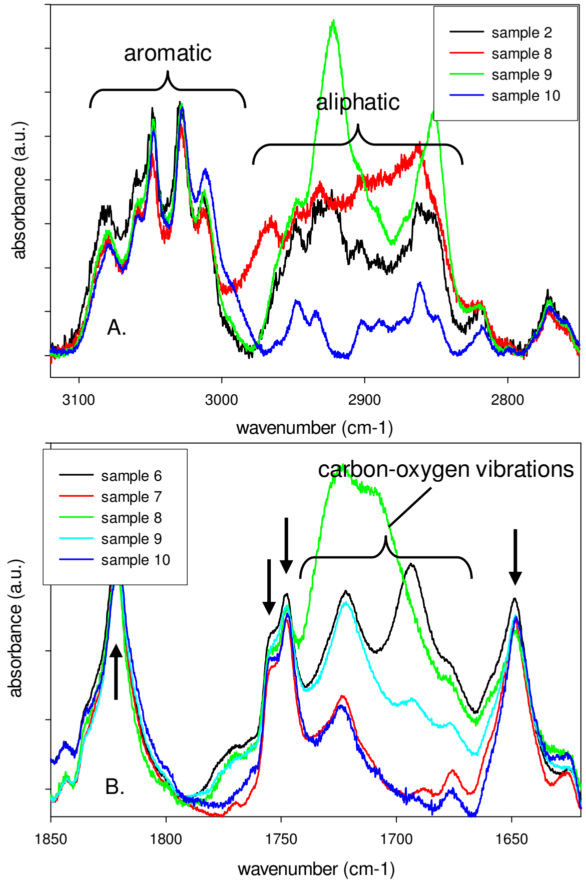

Figure 3. *IR spectra of CuPc samples: A) carbon-hydrogen vibration range and B) carbon-oxygen vibration range. For clarity only few selected samples are shown. A) Aromatic signal is constant for all samples (benzene rings within a CuPc molecule) while aliphatic signal varies among the samples (additives, impurities). B) Arrows mark absorption associated with the CuPc molecules.*

A lack of agreement between the experimental data and the theoretical fit using the binding energies obtained from the thin film measurements is due to presence of carbon containing additives. The presence of the additives is further confirmed by the FTIR measurements. Figure 3A shows the IR spectral range of the aromatic and aliphatic C-H stretching vibrations. While the aromatic C-H signal, resulting mostly from the peripheral CuPc benzene rings, remains the same for all the measured pigments, the aliphatic C-H component varies among the measured pigments indicating presences of additives containing various amounts of aliphatic carbon chains. Similarly a difference among the spectra of different pigments can be seen in the region where carbon-oxygen absorption is present (Figure 3B) showing that additives may consist of species containing different amounts of hydroxyl and carboxyl groups [9].

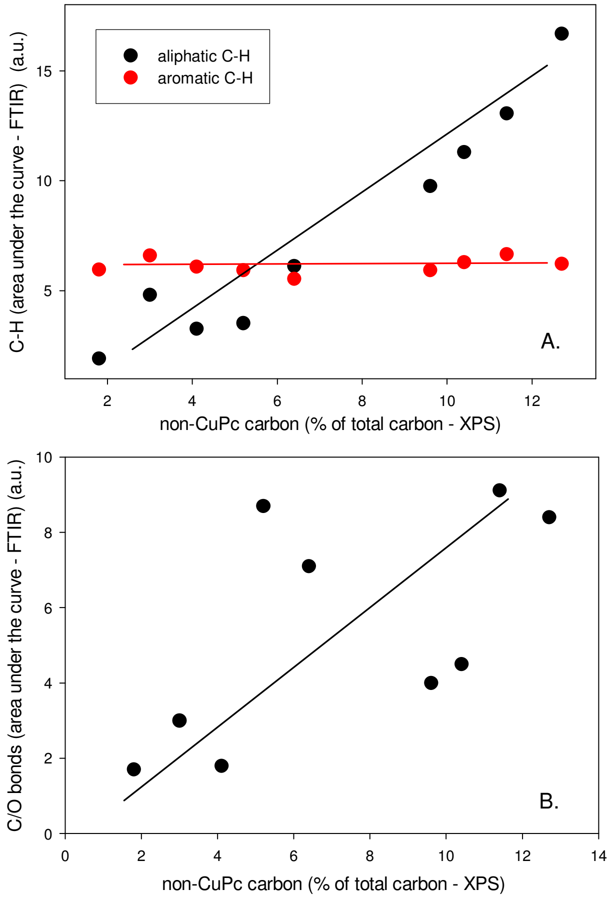

***Figure 4.** A) Correlation between the non-CuPc carbon (as measured by XPS) and C-H aliphatic and aromatic absorption (FTIR). Majority of non-CuPc carbon forms aliphatic C-H bonds. B) Correlation between the non-CuPc carbon (as measured by XPS) and carbon-oxygen IR absorption band between 1600 cm^{-1} and 1800 cm-1. Large portion of non-CuPc carbon forms moieties containing carbon-oxygen bonds.*

Based on this observation, an additional component with binding energy of 285.6 eV was added to the XPS fitting routine and the fitting process was iterated into the satisfactory agreement was obtained for measured samples. The resulting binding energy values for all samples are as follows: C1 = 284.81 eV, C2 = 286.16 eV, SC1 = 286.61 eV, SC2 = 288.17 eV, and the non-CuPc carbon = 285.64 eV. Area under the 285.64 eV peak was then used to quantify the amount of non-CuPc carbon present in the samples. Table 2 summarizes the results demonstrating excellent fit and consistency throughout all the measured CuPc pigment samples.

Comparison of the non-CuPc C1s calculation with the FTIR results shows an excellent agreement with the intensity of the aliphatic C-H vibrations (Figure 4A) and a relatively good correlation with the absoprtion related to carbon-oxygen bond vibration (Figure 4B). It is worth noticing that the best fit of the experimental XPS results requires that the width of the non-CuPc signal (FWHM) is larger than the corresponding values of the CuPc components (Table 2). It implies that the non-CuPc XPS peak is in fact a superposition of many peaks representing different carbon molecular configurations present within the pigment additives. This observation is further supported by the complex nature of the O1s XPS signal observed in the pigments (Figure 5) suggesting presence of a variety of molecular configurations containing carbon-oxygen bonds.

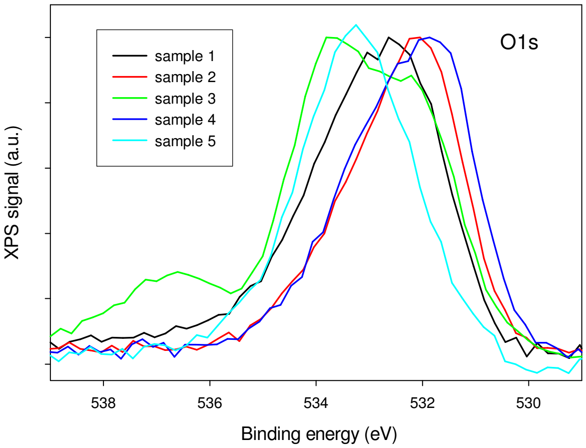

***Figure 5.** O1s XPS spectra of CuPc - for clarity only few selected samples are shown.*

Conclusions

A large number of the commercial CuPc pigments (over 15, different vendors) were analyzed. Detailed analysis of the XPS C1s signal provided very accurate measurement of the binding energies of carbon residing in benzene and pyrrole configurations within the CuPc molecule. In addition, the binding energies of the respective shake-up states were determined. The concentration of the carbon residing in pigment additives (non-CuPc carbon) was quantified and the result agreed with the relative carbon concentration measurement provided by the FTIR analysis. It was found, that for the majority of CuPc commercial pigments, this extraneous carbon was due to impurities containing aliphatic hydrocarbons. This work provides methodology for routine analysis of the CuPc pigments with the help of X-ray photoelectron spectroscopy.

Table.2. Results of the five-peak fitting.

sample		1	2	3	4	5	6	7	8	9	10
Non-CuPc C (% of total C)		6.4	11.4	9.6	12.7	51	3.0	1.8	5.2	10.4	4.1
χ^2		1.44	1.21	1.20	1.12	1.56	1.63	2.10	1.75	1.26	1.40
FWHM	284.81 eV	0.96	1.01	0.98	0.97	1.01	1.00	0.98	0.97	0.96	1.01
	286.16 eV	1.02	1.04	1.02	1. 03	1.02	1.01	1.03	0.99	1.00	1.01
	286.61 eV	1.17	1.19	1.14	1.17	1.18	1.18	1.16	1.18	1.16	1.17
	288.17 eV	0.94	0.97	0.91	0.95	0.94	0.95	0.97	0.95	0.91	0.90
	285.64 eV	1.35	1.44	1.42	1.41	1.88	1.43	1.47	1.48	1.42	1.37
(C1+SC1) / (C2+SC2)		3.01	2.99	3.00	3.02	- [a]	3.00	3.00	3.02	3.01	3.01
SC1 / C1		0.12	0.14	0.12	0.13	- [a]	0.12	0.13	0.12	0.16	0.13
SC2/C2		0.15	0.15	0.15	0.14	- [a]	0.14	0.18	0.12	0.16	0.21

[a] this value could not be accurately determined due to high non-CuPc carbon concentration.

Acknowledgments.

The authors acknowledge fruitful discussion with Eric Hanson, Yan Zhao, Omer Gila and William F. Stickle. Collaboration with many of the commercial organic pigment providers is gratefully acknowledged.

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