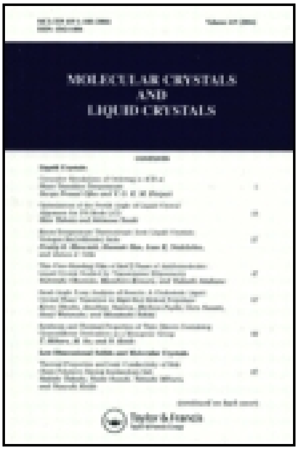

Molecular Crystals and Liquid Crystals

Ultraviolet Photoelectron Spectroscopy of Polymers

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Ultraviolet Photoelectron Spectroscopy of Polymers

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During the past three decades, ultraviolet photoelectron spectroscopy of polymer films has evolved from a sort of appearance-potential (valence band edge) measurement, into a tool for studying the full valence band region of thin polymer films, including insulating polymers, semiconducting polymers and electrically conducting polymers. Progress may be loosely divided into several categories: (A) the melding of thin polymer film technology with ultra high vacuum technology and the widespread use of helium resonance lamps for studies of solid surfaces; (B) the combined approach of measurements and appropriate theoretical-computational methods; and (C) the advent of synchrotron radiation resulting in multi-photon spectroscopies, nominally in the area of the near UV. A coincident discovery of electrically conducting polymers, and especially the evolution of applications of

WRS is grateful to Prof. H. Inokuchi and Prof. K. Seki for the invitation to present this summary at the 54th Fujihara Seminar, in September 2005. The first ultraviolet photoelectron spectroscopy of polymers by WRS was carried out under the auspices of Dr. C. B. Duke, and within the Xerox Webster Research Center, NY, USA. The collaborations with J. L. Brédas on a combined theoretical-experimental approach (and with C. B. Duke, before the terminology "combined theoretical-experimental approach" was ever used) are gratefully acknowledged. M. P. de Jong, W. Osikowicz, and R. Friedlein, are supported by the EU-Integrated Project NAIMO (NAnoscale Integrated processing of self-organising Multifunctional Organic materials, Project number NMP4-CT-2004-500355). Research in Linköping in general is supported by the Swedish Science Foundation (*Vetenskaps Rådet*), the Swedish Foundation for Strategic Research (through the Center for Advanced Molecular Materials, CAMM, and the Center for Organic Electronics, COE), as well as contracts with DuPont Corporation, USA, and Merck Chemicals, UK.

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semiconducting polymers, added technologically driven emphasis to this development of UPS for polymer materials. This contribution traces a limited number of highlights in the evolution of UPS of polymers, from the '70's through to 2005.

Keywords: polymers; ultraviolet photoelectron spectroscopy; UPS

INTRODUCTION

The proceedings article is written for the 54th Fujihara Seminar. The speakers were asked to include at least some sort of historical perspective in their presentations. The written report represents the essential parts of a presentation by one of the authors (WRS), with his perspective on the ultraviolet photoelectron spectroscopy of polymers, which was validated in the question and answer period following the talk. The historical points of view are those of the corresponding author (WRS), and hopefully any omissions will be overlooked.

The state of the art in organic semiconductors was reviewed and celebrated already in 1988 [1]. At that time, on that occasion, it was recognized that photoelectric emission "of negative charges" from organic dyes was noted already in 1888 [2,3], and from anthracene layers already in 1906 [4,5], as discussed by Eley in 1989 [6]. For condensed molecular solids, photoionization thresholds were measured as a means of determining the first ionization potential, in the 1950s [7–10], as discussed by Seki [11]. It also appears that UPS, the energy resolution of photoemitted electrons into "spectra," emerged in the 1960s, principally through the works of Vilesov, and coworkers [12], as well as Turner and coworkers [13]. A review of the evolution of photoelectron spectroscopy from the 1940s through the 1970s is provided by K. Siegbahn, wherein the development of ESCA (Electron Spectroscopy for Chemical Applications) is also discussed, in detail [14].

This brief overview is divided into three parts: The beginnings of the full UPS of polymers; a more-or-less state of the art of polymer UPS today; and one view of the evolution of "UPS" for molecular and polymer hybrid interfaces in the future.

EARLY FULL UPS OF POLYMERS

For polymers, by necessity in thin film form, the earliest works involved appearance potential spectroscopy, looking mostly at the photoelectron emission edge as a function of photon energy [7–10]. Difficulties in obtaining a full ultraviolet photoelectron spectrum involved ultra-thin film sample preparation, and the combination of (ultra-) high vacuum requirements of ultraviolet photoelectron spectroscopy (UPS) with "sample handling," wherein a clean polymer surface could not easily be prepared *in situ*. These experimental requirements came together at the Xerox Webster Research Center in New York in the 1970's, under the guidance of C. B. Duke [15]. Probably the first UPS spectra of (pendant group) polymers [16,17] are shown in Figures 1 and 2. From the time of this work, the UPS of polymers, in ultra-thin film form, has evolved to be a tool of central importance in determining the electronic structure of polymers and hybrid interfaces. An important enabling factor was the close collaboration of theory and experiment in the same studies. This combined approach, although intuitively obvious . . . after the fact . . . was the basis upon which the UPS of polymers became a key factor in determining the electronic structure of polymers for electronics in the future. Starting with the Duke-Salaneck collaborations [18–21] at Xerox in the 1970s,

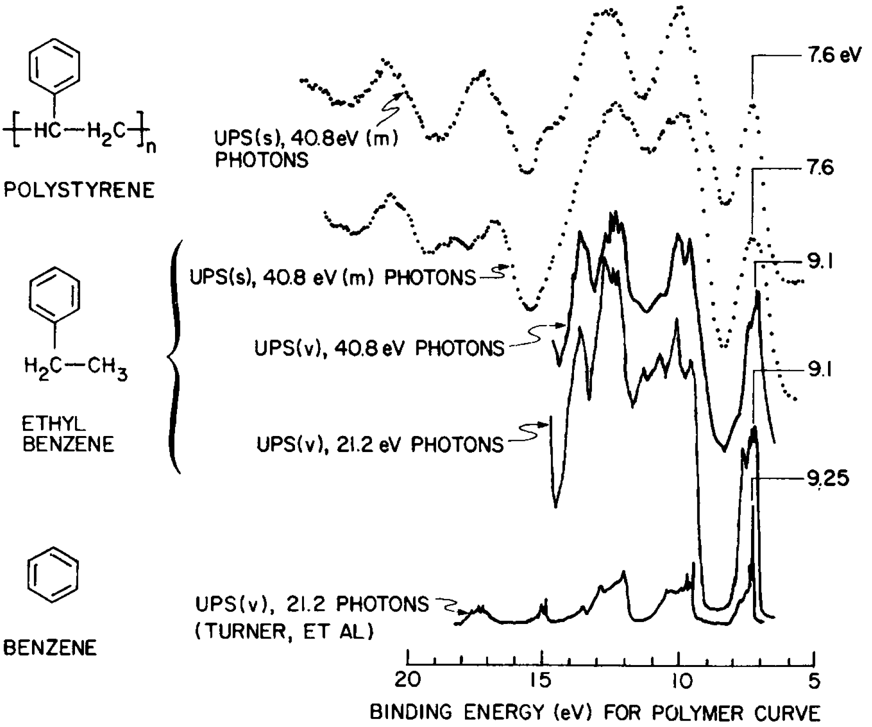

FIGURE 1 The UPS spectrum of polystyrene is shown in comparison with a few reference materials [16,17].

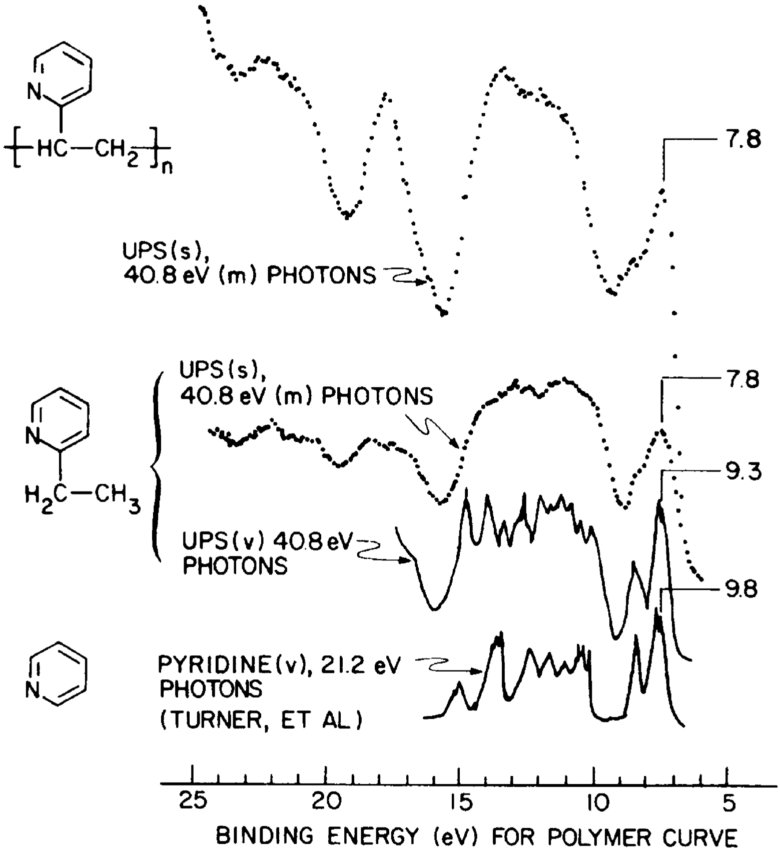

FIGURE 2 The UPS spectrum of polypyridine is shown in comparison with several reference materials [16,17].

and continuing (with enhanced emphasis) with the Brédas-Salaneck collaborations [22,23] since then. The combined theoretical approach represents the added value obtainable through interdisciplinary research (if we may define theoretical physics and experimental physics as “different disciplines”).

RELATIVE STANDARD OF UPS OF POLYMERS TODAY

Space, and an acute fear of missing some important references, prevents the discussion of the full evolution of the UPS of polymers in this paper. However, an important step was the application of UPS to the (then) new electrically conducting polymers [19,24–26],

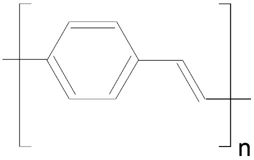

FIGURE 3 The repeat unit (unit cell) of the poly(*p*-phenylenevinylene), or PPV, polymer chain.

and eventually, especially, to studies of the electronic structure of semiconducting polymers for applications in light emitting devices [22], and polymer electronics in general [23]. An example of present conventional UPS works is related below.

What might be termed "conventional UPS" of polymer (thin films) today normally refers to spectra taken in the home laboratories with "conventional" UV light sources, such as the well-developed helium resonance lamp. Two particularly useful lines, He I (21.2 eV Photons) and He II (40.8 eV), are available. In addition, even though the He-lines are well separated in energy, monochromatization with a simple grating filter may be used to remove He I from the He II line, resulting in clean background for the spectra, as discussed in Ref. [27]. In the example chosen, a thin film of a precursor polymer for poly(*p*-phenylenevinylene), or PPV, was thermally converted in ultra-high vacuum (UHV) overnight, resulting in a pure, thin film (approximately 10 nm in thickness), with an ultra pure surface [28], the chemical structure of which is shown in Figure 3. The UPS spectra shown in Figure 4 were obtained with both He I and He II radiation [29], and compared with the results of quantum chemical calculations [30]. Although many such "conventional" UPS spectra are to be found in the literature today, we suggest that those of Figure 4 are representative of the array of spectra in the literature, and reflect the state-of-the-art today. The very good correspondence between the structural features in the experimental spectra and those of the theoretical density-of-valence-states enables a detailed interpretation for the electronic structure of the polymer material [30].

A PEEK AT THE FUTURE

With the advent of synchrotron radiation over through the 1970s up until today, the traditional nomenclature of XPS (X-ray Photoelectron Spectroscopy) and UPS loose meaning. New monochromatic sources enable PES (photoelectron spectroscopy) to be carried out with a wide range of photon energies. Tunable soft X-ray and near UV sources

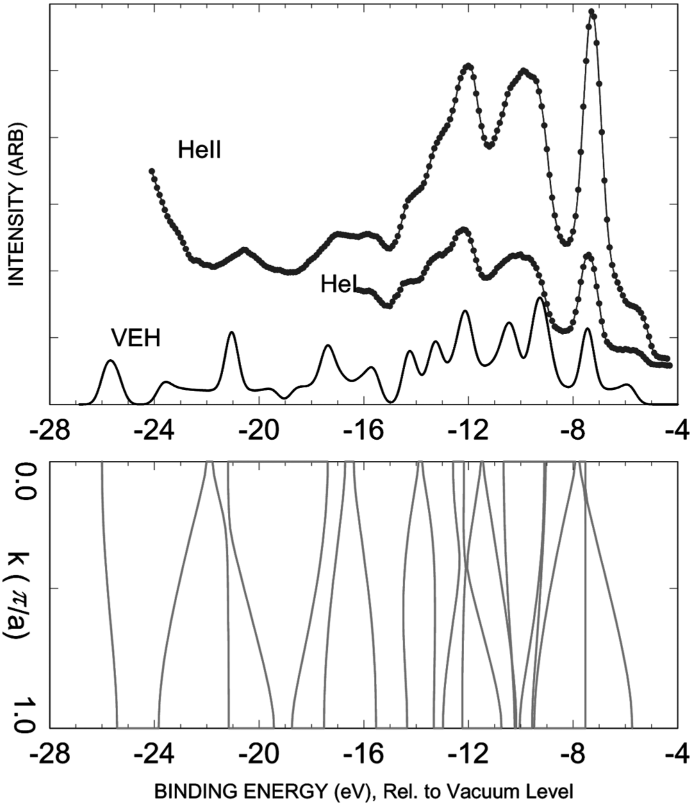

FIGURE 4 The conventional UPS spectra of a polymer that has been a key ingredient in the evolution of polymer electronics, poly(*p*-phenylenevinylene), or PPV [29]. The 1-D band structure for an isolated chain is shown in the lower panel [30], while the k-averaged density of states is derived from the VEH model [34].

enable a wide variety of complex variations of UPS to be carried out. One example will be briefly sketched out below. The example was chosen since it represents a combination of several somewhat exotic aspects of "UPS" that can be done today, in the present case to study fast charge transfer at a hybrid interface for organic electronics.

The materials system is a model layer of Fe(II)-tetraphenylporphyrin, or Fe-TPP, on the surface of a cleaved (flat and clean) MoS_2 substrate [31]. Both the organic layer and the substrate were chosen such that highly ordered condensed molecular films could be obtained, which ultimately provided the possibility to obtain orbital-selective information. The long term goal, and a topic of current research, is

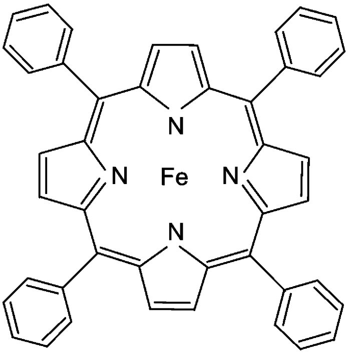

FIGURE 5 The structure of the Fe-TPP molecule.

to extend the method to a wide range of hybrid interfaces occurring in organic (polymer)-based electronic applications. The molecular structure of the Fe-TPP molecule is shown in Figure 5.

By doing soft X-ray absorption (sometimes denoted as near edge x-ray absorption fine structure, NEXAFS), electronic transitions from a specific core-electron state, e.g., C(1s) in the present case, can be made. The electron in an excited state of the molecule may decay by any of several non-radiative decay modes. In the one mode of importance here, the electron decays to fill the hole from which it came, in turn giving the de-excitation energy to an electron in one of the occupied valence levels of the molecule. The decay event leaves a hole in the valence level, and is formally equivalent to the single-hole final-state generated in normal UPS.

In Figure 6 is illustrated the relevant electronic levels for discussing the experiment: The soft X-ray excitation process (A), the aforementioned decay mechanism, participator decay (B), and a competing decay mechanism, spectator decay (C), which is largely disregarded in the present context. The energy distribution of the escaping electrons in B is equivalent to a “UPS” spectrum, or so-called Resonant Photoelectron Spectrum, RPES, although the cross sections in RPES are usually strongly enhanced as compared to UPS. Diagram D illustrates that when the molecule is on a metallic substrate there may be a chance for an additional decay channel, charge transfer to the substrate, which would compete with the resonant processes B and C. If charge transfer does occur on the time scale of the core-hole life time (while the electron is still in the excited state), then the corresponding peak in the RPES will be reduced compared to that in the RPES of a thicker layer of molecules, where events at the interface with the

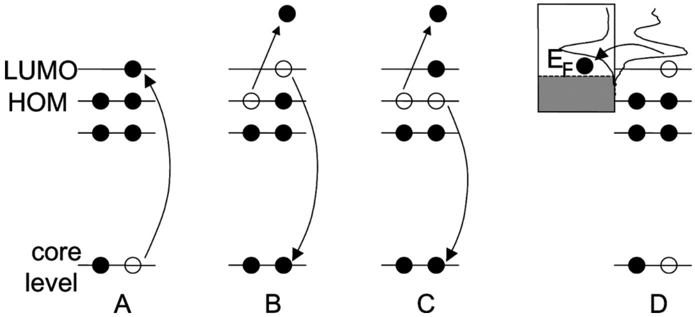

FIGURE 6 The diagrams illustrate: The soft X-ray excitation process (A), the decay mechanism of interest, participator decay (B), and a competing decay mechanism, spectator decay (C). Diagram D illustrates that when the molecule is on a metallic substrate there may be a chance for an additional decay channel, charge transfer to the substrate, which would compete with B and C. The energy distribution of the escaping electrons in B compromises a Resonant "UPS" spectrum, RPES.

substrate are not visible, because of the short elastic- mean-free-paths of low energy electrons in organic molecular solids [32]. A detailed discussion, with an analysis of the soft X-ray absorption, the RPES, and the resultant charge transfer rates from specific molecular states are to be found in the original paper [31]. However, in Figure 7 are shown three sets of RPES spectra, recorded following the excitation of electrons from the C(1s) level of the Fe-TPP molecules, using 284.3, 285.1 and 285.5 eV soft X-ray photons. At 285.1eV, electrons are put into a group of initially unoccupied molecular orbitals localized on the prophryn ring (A), while with 285.5 eV photons, electrons are put into initially empty orbitals localized on the phenyl-end-groups (B) of the Fe-TPP molecules. The solid lines are for thick molecular films, where the effect of charge transfer to the substrate can not be seen, whereas the dotted lines are for the monolayer of Fe-TPP molecules on the substrate. It can clearly be seen that during the life time of the core hole, some electrons in orbitals B are lost to the substrate, and at a different rate depending upon how high up in energy the X-rays put them. Suffice it to say here that two different (sets of) molecular orbitals could be addressed selectively via soft X-ray absorption, and that the specific orbital-dependent charge transfer rates to the substrate could then be estimated to be >30 femto-seconds in one case (orbitals A) and about 3 to 6 femto-seconds in another case (orbitals B). These fast charge transfer rates are estimated form what is essentially a "dc" experiment, due to the concept of the "core hole clock" [33]. The

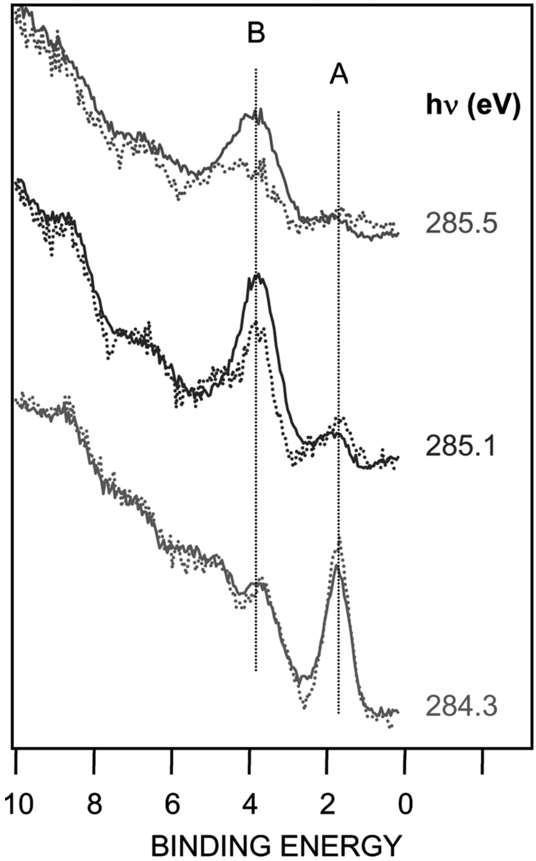

FIGURE 7 RPES spectra, following soft X-ray excitation of electrons into several different, separable molecular states, of the Fe-TPP molecules on the surface of MoS_2 [31]. The dotted lines (. . .) are the spectra for the monolayer on MoS_2, while the solid lines are for a thick layer, where the effects of the substrate are not seen.

complex nature of the measurements, and the need for sophisticated photon sources, is only one representation of the evolution to “Big Science” of the humble “in-house” UPS method, over the past 30 years.

REFERENCES

[1] Inokuchi, H., Sano, M., Maruyama, Y., & Sato, N. (1989). Proceedings of the OJI international seminar on organic semiconductors-40 years. *Mol. Cryst. Liq. Cryst.*, *171*, 1–356.

[2] Stoletow, A. (1888). *Comptes Rendus*, *106*, 1149.

[3] Stoletow, A. (1888). *Comptes Rendus*, *106*, 1593.
[4] Pocchetino, A. (1906). *Atti Accad. Lincei*, *15*, 335.
[5] Pocchetino, A. (1906). *Atti Accad. Lincei*, *15*, 171.
[6] Eley, D. D. (1989). Studies of organic semiconductors for 40 years-I: The mobile π-electron 40 years on. *Mol. Cryst. Liq. Cryst.*, *171*, 1–21.
[7] Watanabe, K., Nakayama, T., & Mottle, J. (1962). *J. Quant. Spectrosc. Energy Transf.*, *2*, 369.
[8] Terenin, A. & Vilesov, F. I. (1964). *Adv. Photochem.*, *2*, 285.
[9] Vilesov, F. I. (1963). *Usp. Fiz. Nauk.*, *81*, 669.
[10] Vilesov, F. I. (1964). *Sov. Phys. USPEKHI*, *6*, 888.
[11] Seki, K. (1989). Ionization energies of free molecules and molecular solids. *Mol. Cryst. Liq. Cryst.*, *171*, 255–270.
[12] Vilesov, F. I., Kurbatov, B. L., & Terenin, A. N. (1961). *Dokl. Akad. Nauk SSSR*, *138*, 1329.
[13] Turner, D. W., Baker, C., Baker, A. D., & Brundle, C. R. (1970). *Molecular Photoelectron Spectroscopy*, Wiley: London.
[14] Siegbahn, K. (1982). Electron spectroscopy for atoms, molecules, and condensed matter. *Science*, *217*, 111–121.
[15] Duke, C. B., Salaneck, W. R., Fabish, T. J., Ritsko, J. J., Thomas, H. R., & Paton, A. (1978). Electronic structure of pendant-group polymers: molecular-ion states and dielectric properties of poly(2-vinyl pyridine). *Phys. Rev. B*, *18*, 5717–5739.
[16] Salaneck, W. R. (1980). *Polymer Preprints*, *21*, 119.
[17] Salaneck, W. R. (1981). Characterization of molecular structure of polymers by photon, electron and ion probes. In: *Am. Chem. Soc.*, Fabish, T. J., Dwight, D., & Thomas, H. R. (Eds.), Washington D.C., 121–149.
[18] Duke, C. B., Lipari, N. O., Salaneck, W. R., & Schein, L. B. (1975). The electronic structure of 1,2-di(p-tolyl)ethane and of pure and substituted [2.2] paracyclophane. *J. Chem. Phys.*, *63*, 1758.
[19] Duke, C. B., Paton, A., Salaneck, W. R., Thomas, H. R., Plummer, E. W., Heeger, A. J., & MacDiarmid, A. G. (1978). Electronic structure of polyenes and polyacetylene. *Chem. Phys. Lett.*, *59*, 146.
[20] Duke, C. B., Salaneck, W. R., Fabish, T. J., Ritsko, J. J., Thomas, H. R., & Paton, A. (1978). The electronic structure of pendant-group polymers: molecular ion states and dielectric properties of poly (2-vinyl pyridine). *Phys. Rev.*, *B18*, 5717.
[21] Duke, C. B., Lin, J. W.-p., Paton, A., Salaneck, W. R., & Yip, K. L. (1979). The geometry of cation radicals: the structure of triphenylamine in the condensed versus the vapor phase. *Chem. Phys. Lett.*, *61*, 402.
[22] Salaneck, W. R., Stafström, S., & Brédas, J. L. (1996). *Conjugated Polymer Surfaces and Interfaces*, Cambridge University Press: Cambridge.
[23] Salaneck, W. R., Seki, K., Kahn, A., & Pireaux, J.-J. (Eds.) (2002). *Conjugated Polymer and Molecular Interfaces: Science and Technology for Photonic and Optoelectronic Applications*, Marcel Dekker: New York.
[24] Salaneck, W. R., Thomas, H. R., Duke, C. B., Paton, A., Plummer, E. W., Heeger, A. J., & MacDiarmid, A. G. (1979). Photoelectron spectra of AsF doped polyacetylenes. *J. Chem. Phys.*, *71*, 2044–2050.
[25] Salaneck, W. R., Thomas, H. R., Bigelow, R. W., Duke, C. B., Plummer, E. W., Heeger, A. J., & MacDiarmid, A. G. (1980). Photoelectron spectroscopy of iodine-doped polyacetylene. *J. Chem. Phys.*, *72*, 3674–3678.
[26] Salaneck, W. R. (1985). Photoelectron spectroscopy of the valence electronic structure of polymers. *CRC Critical Reviews in Solid State and Materials Sciences*, *12*, 267–296.

[27] Salaneck, W. R., Bergman, R., Sundgren, J.-E., Rockett, A., Motooka, T., & Greene, J. E. (1988). Adsorption of tri-methyl aluminum molecules on silicon. *Surf. Sci.*, *198*, 461–472.

[28] Andersson, A., Kugler, T., Lögdlund, M., Li, A. B. H. X., & Salaneck, W. R. (1999). Buried interfaces: Interfacial interactions in materials for polymer-LED applications. *Surf. Interf. Analysis*, *28*, 186.

[29] Salaneck, W. R., Kugler, T., Andersson, A., Bröms, P., Birgerson, J., & Lögdlund, M. (1999). Conjugated oligomers, polymers, and dendrimers: From polyacetylene to DNA. In: Brédas, J. L. (Ed.), De Boeck & Larcier s. a., Bruxelles, 43–59.

[30] Lögdlund, M., Salaneck, W. R., Meyers, F., Brédas, J. L., Arbuckle, G., Friend, R. H., Holmes, A. B., & Froyer, G. (1993). Evolution of the electronic structure in a conjugated polymer series: polyacetylene, poly(p-phenylene), and poly(p-phenylenevinylene). *Macromolecules*, *26*, 3815.

[31] Jong, M. P. d., Friedlein, R., Sorensen, S. L., Öhrwall, G., Osikowicz, W., Fahlman, M., & Salaneck, W. R. (2005). Orbital specific dynamic charge transfer from Fe(II)-tetraphenylporphyrin molecules to molybdenum disulfide substrates. *Phys. Rev. B*, *72*, 035448.

[32] Salaneck, W. R. (1978). *Phys. Rev. Lett.*, *40*, 60.

[33] Schnadt, J., Brühwiler, P. A., Patthey, L., O'Shea, J. N., Södergren, S., Odelius, M., Ahuja, R., Karis, O., Bässler, M., Persson, P., Siegbahn, H., Lunell, S., & Mårtensson, N. (2002). *Nature*, *418*, 620.

[34] Brédas, J. L., Chance, R. R., Silbey, R., Nicolas, G., & Durand, P. (1981). *J. Chem. Phys.*, *75*, 255.