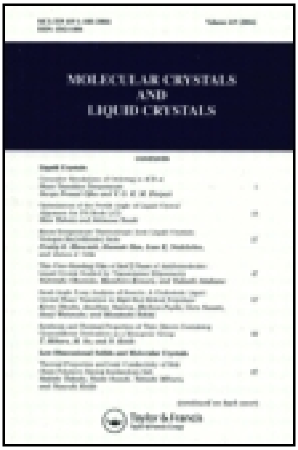

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

UV-Photoelectron Spectroscopy of One- and Two Component Organic Crystals

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To cite this article: Norbert Karl & Naoki Sato (1992): UV-Photoelectron Spectroscopy of One- and Two Component Organic Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 218:1, 79-84

To link to this article: http://dx.doi.org/10.1080/10587259208047019

Mol. Cryst. Liq. Cryst. 1992, Vol. 218, pp. 79–84
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Printed in the United States of America

UV-PHOTOELECTRON SPECTROSCOPY OF ONE- AND TWO-COMPONENT ORGANIC CRYSTALS

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Abstract For potential applications of organic materials as active components in electronics, the energetic position of their valence and conduction levels are important parameters. For a given parent molecule, e.g. an aromatic hydrocarbon, the positions of these levels can be shifted substantially by attaching donor- or acceptor-type side group units. This will be demonstrated for the perylene skeleton in perylene-3,4,9,10-tetracarboxylic-dianhydride, N,N'-diphenyl-perylene-3,4,9,10-tetracarboxylic-diimide, and diindeno[1,2,3,-*c,d*:1',2',3'-*lm*]perylene. Energy level manipulation by introducing donor:acceptor ground state interactions is another possible concept which has been checked with ***single crystals*** of the stoichiometric donor:acceptor complexes tetrathiafulvalene:p-chloranil, phenothiazine:tetracyanoquinodimethane, phenothazine:pyromellitic-dianhydride, perylene:pyromellitic-dianhydride and perylene:tetracyanoquinodimethane, where a certain dark conductivity or light-induced photoconductivity served to eliminate charging problems.

INTRODUCTION

The prospect of using ***organic molecular*** materials for potential future applications as active components in electronics has only recently attracted widespread attention, leading to a real rush of ideas and suggestions, see e.g. ref. 1, although the physical basis of dark[2,3] and photoconductivity[3] in this class of materials, including quasi-metallic conductivity[2] and even superconductivity[4], have been the subject of a great number of investigations for a considerable while[5].

For the conception and design of well-defined model systems, a detailed knowledge of the energetic position, gained under well controlled conditions, of the valence and conduction levels ("ionic energy levels") of their components is indispensable. Such knowledge can be obtained by ultraviolet photoelectron spectroscopy (UPS). UPS results, in addition, can provide information on possible manipulations, suitable for shifting and fine-adjustment of these levels, and thus allow an optimization of desired properties.

Two complementary ways of manipulating ionic energy levels in molecular π-electron systems have been followed in this work: (1) *Intramolecular* modifications by attaching suitable donor- or acceptor-type substituents, and (2) modifications by introducing *intermolecular* ground state charge transfer interactions by complexation with suitable electron donor or electron acceptor partners.

Following the first of these guidelines we have chosen representatives of the large family of molecules containing the perylene core as a central backbone unit, viz. perylene-3,4,9,10-tetracarboxylic-dianhydride (PTCDA), N,N'-diphenyl-perylene-3,4,9,10-tetracarboxylic-diimide (DP-PTCDI), and diindeno-[1,2,3,-*c*,*d*:1',2',3'-*lm*]perylene (DIP). Each of these materials combines a very low room temperature vapor pressure with high thermal stability, allowing its deposition from the vapor phase under ultrahigh vacuum conditions, including the possibilty of *molecular beam epitaxy*. The ligands to the perylene core selected with these representatives span a wide range from more electron accepting (PTCDA) to more electron donating (DP-PTCDI, DIP) nature. Because these materials are insulators in the dark, which would cause serious charging problems in UPS if they were employed in bulky form, we used sufficiently thin films on copper substrates as samples.

With the second guideline in mind we chose several stoichiometric donor:acceptor *single crystals*, tetrathiavulvalene:p-chloranil(TTF:CA), phenothiazine:tetracyanoquinodimethane(PTZ:TCNQ), phenothiazine:pyromellitic-dianhydride(PTZ:PMDA), perylene:pyromellitic-dianhydride(PER:PMDA), and perylene:tetracyanoquinodimethane (PER:TCNQ), and determined the shift of their ionization threshold energy upon complexation, by comparison with the ionization threshold of the respective pure donor solid. The use of single crystals of the complexes is crucial here, because neither co-evaporation of the components nor evaporation of the complex can guarantee a deposition of thin films of the *stoichiometric complex phase*, except, perhaps, under very carefully selected conditions[6]. (Neverthless, the level shifts upon complexation, to be studied here, were initially detected with thin film samples, cf. ref. 7.)

EXPERIMENTAL

Thin film samples for UPS, several ten nanometers thick, were prepared on copper substrates as described before[8]. Donor:acceptor single crystals were grown from the vapor phase under near isothermal conditions using the plate sublimation technique[9]. Several crystals of each batch were placed together in close proximity and attached to the copper support covered with fresh silver paint by touching them from above. To improve the resolution of the UP spectra, it turned out to be useful to expose a fresh surface from time to time, obtainable by treating the crystal surfaces with a soft (stainless steel) wire brush. The UPS measurements were made with different photon energies (obtained from a Hinteregger-type hydrogen discharge lamp) by measuring (differential) yield as a function of retarding potential with a lock-in technique as described in more detail elsewhere[8]. In the figures to be presented the original retardation potential spectra are rearranged on an ionization potential scale (ordinate), with zero of the electron binding energy at the vacuum level and with the differential yield η potted on the abscissa, with an offset for each spectrum. The threshold energy for photoemission, I^{th}, which indicates the upper edge of the valence band, is marked by a dashed line.

RESULTS AND DISCUSSION

Photoelectron spectra of PTCDA and DIP are presented in Figures 1 and 2. These results show that already the conventional stable substituents, chosen in these examples, lead to a difference of the ionization thresholds, and hence of the upper valence band edges, of as much as 1.0 eV.

For single crystals of the donor:acceptor complex PER:TCNQ, a photoionization threshold energy of 5.51(9)eV was determined from 11 photoelectron spectra at photon energies between 7.29 and 9.18 eV. In comparison with single crystal spectra of a pure PER crystal[10], where by illumination with lower photon energy light sample charging could essentially be eliminated (though not fully, see horizontal bars in Fig. 3, indicating the residual drift), there is a complexation shift of ~0.4 eV to higher binding energy, cf. Fig. 3, which we attribute to an additional binding of the electron to the donor PER molecule (from which it is to be removed) by ground state charge transfer ineractions with the adjacent acceptor (TCNQ) molecules, based on the large electron affinity of the latter.

The results obtained for all materials studied are collected in Table 1. These data clearly reflect that (I) the ionization threshold energy of a donor: acceptor *complex* is determined by the HOMO (highest filled molecular orbital) of the *donor*, and (II) the ionization threshold energy of the donor molecule increases by *intermolecular* charge transfer (CT) interactions with the surrounding acceptor molecules. These increases are smaller, however, than those obtainable through *intramolecular* charge transfer upon introduction of suitably selected substituents: While the latter can lead to a shift of the order of 1eV, intermolecular ground state donor—acceptor type CT-interactions can only provide energy shifts of a few tenths of an eV.

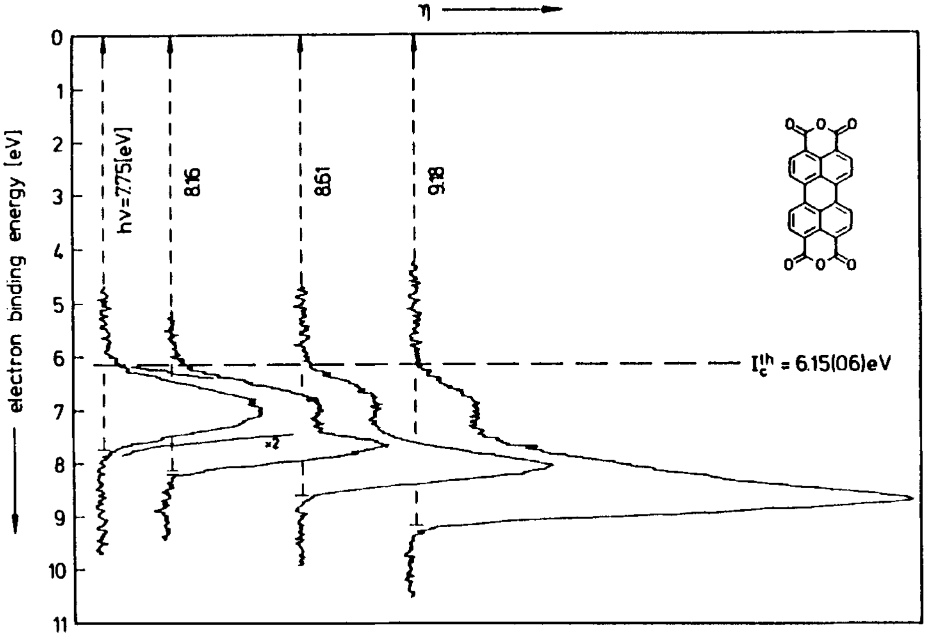

FIGURE 1 Photoelectron spectra of a thin film of perylenene-tetracarboxylic-dianhydride (PTCDA), measured at the different photon energies indicated.

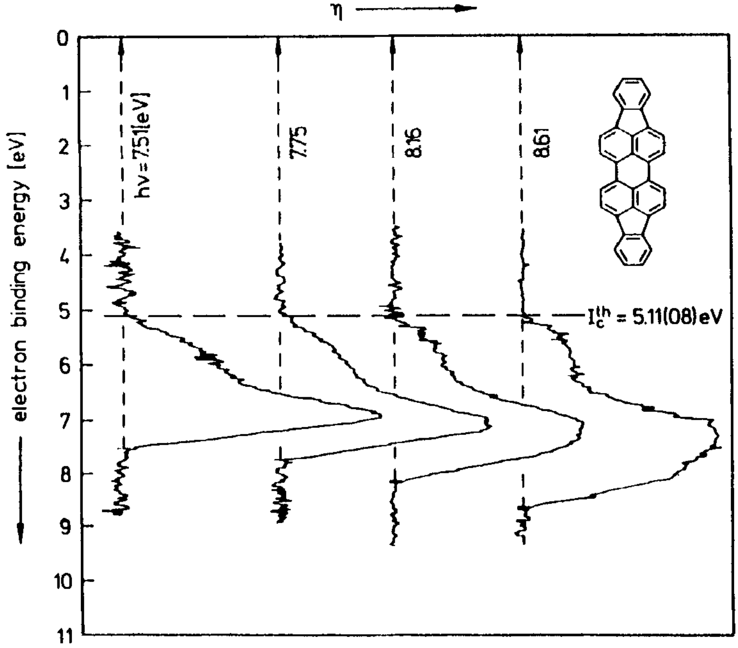

FIGURE 2 Photoelectron spectra of a thin film of diindeno-perylene (DIP).

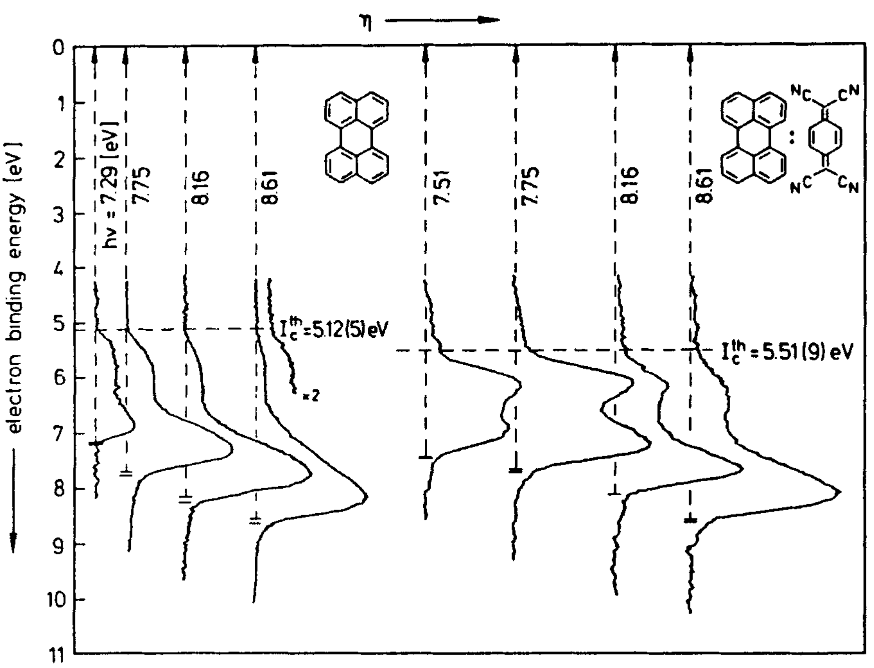

FIGURE 3 Several photoelectron spectra of a single crystal of perylene, and of the perylene:TCNQ 1:1 donor:acceptor complex, arranged together for showing the difference of their ionization threshold energy values.

TABLE I Ionization threshold energies [eV] obtained (I) with thin films of several perylene derivatives, and (II) with stoichometric single crystals of donor:acceptor complexes (in comparison with those of the pure single crystals). These ionization energies are systematically increased by *intramolecular* (I) and by *ground state intermolecular* (II) charge transfer interactions.

I			DIP	5.11 (8)		
			DP–PTCDI	5.99(9)		
			PTCDA	6.15(6)		
II	TTF	~5.0[10]*	PTZ	5.15 (5)[10]	PER	5.12(5)[10]
	TTF:CA	4.93(6)	PTZ:TCNQ	5.28(6)	PER:TCNQ	5.51(9)
			PTZ:PMDA	5.38(9)	PER:PMDA	5.50(11)

*Polycrystalline thin film: no single crystal value available yet. There is a general trend, however, that I^{th} energies of single crystals are smaller by 0.1-0.2eV than those of polycrystalline or disordered thin films[10].

In summary, we have shown that manipulations of charge transfer interactions, both of intra- and of intermolecular nature, can be used to shift energy levels of organic photo- and semiconductors on an absolute scale (i.e. relative to vacuum level) and hence also relative to one another. This aspect is especially important for tailoring barriers, such as e.g. Schottky barriers, or barriers at organic/organic interfaces used for light-induced electron—hole separation (photovoltaic solar energy conversion), or for obtaining Ohmic or injecting contacts, etc., cf. refs. 12 and 13.

Acknowledgments
The authors wish to thank Prof. H. Inokuchi who made this cooperation possible. We also gratefully acknowledge the cooperation of B. M. Schmid and H. Yamamoto.

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