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Probing charge transfer dynamics in self-assembled monolayers by core hole clock approach

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ABSTRACT

This article reviews recent progress in the application of core hole clock approach in the framework of resonant Auger electron spectroscopy to the monomolecular assembles of alkyl, oligophenyl, and oligo(phenylene–ethynylene) based molecules on Au(1 1 1) substrates, referring mostly to the work by the author et al. The major goal was to study electron transfer (ET) dynamics in these systems serving as prototypes of molecular electronics (ME) devices. The ET pathway to the conductive substrate was unambiguously defined by resonant excitation of the nitrile tailgroup attached to the molecular backbone. Characteristic ET times within the femtosecond domain were determined, along with the attenuation factors for the ET dynamics, analogous to the case of the static transport. The above parameters were found to exhibit strong dependence on the character of the molecular orbital which mediates the ET process. In addition, certain spectral features, which can be associated with an inverse ET from the molecular backbone to the excitation site, were observed upon exchange of the nitrile group by strongly electronegative nitro moiety. The reported results represent a valuable input for theory and a certain potential for applications such as ME devices where optimization of ET can have significant technological impact.

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1. Introduction

Charge transport through individual molecular units, including so called "molecular wires" (MWs), is an important issue, in particular, for such frontier fields of modern science and technology as molecular and organic electronics as well as organic photovoltaics [1–3]. In this context, significant activity regarding the investigation of transport properties of potential MWs and prototype molecules has evolved [2,4]. These moieties were addressed both individually and as a molecular assembly on conductive substrates, bonded over a dedicated anchor group. The most popular experimental strategies included the use of conducting probe atomic force microscopy and scanning tunneling microscopy [5–13], break junction techniques [14–19], in-wire junctions [18], mercury drop approach [20–24], and liquid metal eutectic Ga–In top contact [25]. A widely used approach is to study a particular series of molecules in a dedicated experiment, varying certain parameters such as the length of molecular chain [4], its conformation [26–29], character of the anchor group (groups) [13], or the work function of the substrate [7,13]. A variety of valuable information was obtained, even though with a certain data scattering related to the basic limitations of particular experiments such as (i) undefined quality of the molecular assembles studied, (ii) uncertainty in the number of molecules participating in the current transport, (iii) uncertainty in the exact shape of the nanoelectrodes used to contact the molecules [30,31], and (iv) non-defined quality of the top contact in the case of molecular assembles (the bottom contact was then provided by the conductive substrate). It turned out, as could be expected, that MWs are generally bad conductors, relying on either nonresonant superexchange tunneling or hopping mechanism [2]. In the former case, the transport properties depend on the internal coupling between the building units of a MW, whereas, in the latter case, charge transport efficiency is affected by the exact position of the mediating state with respect to involved molecular orbitals (MOs) [2,4,5,7,12,20,21]. In most cases, transport properties of MWs could be well described by the equation, $J = J_0 \exp(-ß l)$, where J is the current through a metal–molecule–metal junction, J_0 is a parameter closely related to the molecular contact resistance, ß is an attenuation factor, and l is the length of the molecular backbone [2]. The value of ß depends on the identity of MW. The lowest values, corresponding to a better conductance, were observed for unsaturated hydrocarbon chains such as alkenes ($\beta = 0.27$ Å^{-1} [32]), oligoacenes ($\beta = 0.2$ and 0.5 Å^{-1}, depending on the anchoring [13]), oligo(phenylene ethynylenes)

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(OPE; $\beta \approx 0.3$ Å^{-1} [32,33]), and oligophenyls (OPh, $\beta = 0.41–0.7$ Å^{-1} [2,5,9,20,33]). Saturated hydrocarbon chains such as alkanes are characterized by noticeably higher β values of 0.6–1.0 Å^{-1} [21,33] corresponding to inferior charge transport properties. Significantly lower values of ß (down to 0.001 Å^{-1}) could only be obtained for MWs with incorporated metal centers, because of the specific alignment of the MOs involved or resonant tunneling [34,35]. In many cases, in depth analysis of the experimental data was performed, providing information on the character and specific characteristics of the charge transfer and correlating these parameters with the electronic structure of the systems studied (see e.g. [13,25,34,35]).

All the above knowledge and results refer, however, to the static properties of potential MWs, whereas the quantitative dynamics of charge transport through these "wires" and prototype molecules assembled on or between conductive electrodes has been largely unexplored. This possibility is, however, provided by advanced X-ray spectroscopy, viz. by resonant Auger electron spectroscopy (RAES) within so-called core hole clock (CHC) approach [36]. This approach relies on the resonant excitation of a core electron into a bound state of a molecule or a specific functional group weakly coupled to continuum by a narrow-band X-ray radiation, with the subsequent monitoring of the decay spectra. The basic schematic of the excitation–deexcitation processes behind the CHC approach is presented in Fig. 1. Following the primary excitation into a bound state (**1**) and related intershell transition (**2**), either the excited electron or an electron from the occupied valence levels (OV) can be emitted (**3**), described as participator (P) or spectator (SP) decay, respectively. Both these processes result in characteristic final states with one hole in OV (P) or two holes in OV but an electron in the unoccupied valence levels (UV), corresponding to one hole in total. Alternatively, transfer of the excited electron to a continuum (C) can occur (2′) during the lifetime of the excited state, with the continuum represented mostly by the conductive substrate in the case of adsorbate assembles. Significantly, this route leads to the same final state with two holes in OV as the non-resonant Auger process (A). The latter process involves the excitation of a core electron into a continuum state (**1**) followed by the intershell transition (**2**) and the emission of UV electron (**3**). Note that when the bandwidth of the exciting radiation in the case of RAES is narrower than the core hole lifetime broadening of the neutral core-excited state, it is not possible to disentangle the excitation/de-excitation processes as subsequent steps, but the whole event should be considered as a one-step process with excitation and de-excitation taking place simultaneously [37]. This condition was almost fulfilled in most of our experiments (see Section 2), so that the individual steps in Fig. 1 should be considered as parts of a one-step process.

The spectra characteristic of the different scenarios within the RAES process differ from each other. Whereas a combination of the SP and P events provides a purely resonant spectrum, the spectra signature of the electron transfer (ET) scenario is almost identical with that of the non-resonant Auger process. Consequently, as far as the purely resonant and non-resonant Auger spectra can be measured separately and are sufficiently different, RAES spectrum can be decomposed into the contributions related to the SP + P and ET scenarios, denoted as P_{SP+P} and P_{ET}, respectively, and the ET time (τ_{ET}) can be obtained from the relation $\tau_{\mathrm{ET}} = \tau_{\mathrm{core}}(1 - P_{\mathrm{ET}})/P_{\mathrm{ET}}$, where τ_{core} is the known lifetime of inner shell vacancy [36]. This lifetime is used as an internal time reference – core hole clock – for the ET time. Since τ_{core} is just few fs for inner shell vacancies in atoms common to organic molecules [38–41], this approach offers time resolution in the fs and sub-fs range, in addition to atom-selective charge injection associated with the specific, resonant excitation. It is however limited by τ_{ET} values of 120–150 fs, since the corresponding P_{ET} is then too small to be well perceptible in the decay spectrum.

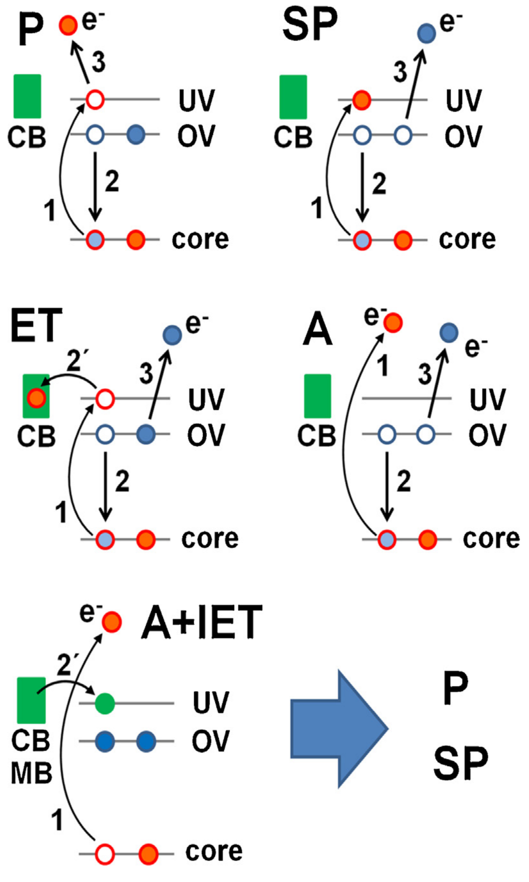

Fig. 1. A schematic of core electron excitation/de-excitation scenarios for the resonant and non-resonant excitation of a functional group weakly coupled to a continuum represented, in most cases, by the conduction band (CB) of the substrate and, in some cases, by molecular backbone (MB), with IS, OV and UV denoting inner shell, occupied and unoccupied valence levels, respectively. P, SP, ET, A, and A + IET denote participant decay, spectator decay, electron transfer, non-resonant Auger process, and inverse electron transfer, respectively. See text for a detailed explanation. Filled and hollow circles represent electrons and holes, respectively, with red and blue color-code corresponding to IS and OV/UV, respectively. Individual steps within particular scenarios are marked by numbers, viz. **1**—primary excitation, **2′**—electron transfer to a continuum, if it occurs; **2**—intershell electron transition; **3**—emission of Auger electron. The numbers are marks only and do not reflect any sequence; the entire excitation/de-excitation event is considered as a one-step process.

The CHC method has been successfully utilized to study molecular adsorbates as well as atomic and molecular films on different substrates, see e.g. [42–47], entering even an attosecond time domain by focusing on short-lived holes with initial and final states in the same electronic shell [48]. Among other systems, this approach, was also applied to MWs, adsorbed as self-assembled monolayers (SAMs) on gold substrates, including thiolate-bonded OPh [49] and OPE [50] films. For these monolayers, backbone-to-substrate ET – if energetically allowed – was found to proceed extremely fast, either on the same time scale as the C 1s core-hole lifetime, 6 fs [49], or even faster, on the time scale below the above lifetime [50]. Unfortunately, the excitation site in terms of a distinct carbon atom on the molecular wire was not defined, which made a numerical evaluation of the experimental data hardly possible.

This problem could be however solved by specific molecular design suggested by us recently [51] and illustrated in Fig. 2. This design allows to define the ET pathway precisely, by attachment of a specific group, which can be resonantly excited by X-rays, to the molecular backbone. Accordingly, the ET time from this tail group to the substrate, through the backbone and across the headgroup-substrate anchor can be precisely measured, unless ET occurs to the

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