

Internal electric fields in vacuum-evaporated organic films as studied by electroabsorption spectroscopy

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Abstract

Electroabsorption (EA) spectroscopy (Stark effect spectroscopy) has been applied to provide information on the internal electric fields occurring in thin films of organic compounds sandwiched between two semitransparent aluminium electrodes (Al/organic film/Al/glass substrate) under ambient conditions. A wide range of molecular materials, commonly used in organic light-emitting diodes, has been investigated. The analysis of the (1ω) EA signals measured on the first harmonic of the applied sinusoidal electric field frequency (ω) indicates a sample asymmetry and the presence of internal electric fields (F_i) in organic films with estimated values of F_i between 4×10^4 and 3×10^5 V/cm. The possible origin of internal electric fields is discussed. The observed features of F_i can be consistently explained by the asymmetrical distribution of space charge in the organic film associated with different defect (of structural and/or impurity origin) characteristics on the substrate and non-substrate side of the sample.

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1. Introduction

Electroabsorption (EA) spectroscopy (Stark effect spectroscopy) is commonly used to infer the charge redistribution in excited molecular systems due to interaction of molecular dipoles with electric field (for a recent review see [1]). Typically, in the EA experiment a sinusoidal voltage, $U_0 \sin(\omega t)$, is applied to the sample and the change, $\Delta\alpha$, in the optical-absorption coefficient is detected synchronously at the second harmonic (2ω). In this case, a quantitative analysis of (2ω) EA spectra allows to characterize excited states of molecular systems and determine their molecular parameters (permanent dipole moment change, Δm , and polarizability change, Δp , upon photoexcitation). However, in non-isotropic or asymmetric systems the EA signals also appear at the first harmonic (1ω) of the applied

electric field frequency. Two main reasons for (1ω) EA effect should be mentioned: linear electrochromism occurring in polar ordered systems like Langmuir–Blodgett films [2] and quasi-linear electrochromism caused by permanent internal electric fields (F_i) existing in the samples [3]. The internal (built-in) electric field F_i may have several origins: (i) the interfacial potential barriers, particularly, due to the work function difference of electrodes [4–7] or interfacial dipoles [8], (ii) space charge occurring in the sample [9–13] or (iii) oriented molecular dipoles in polar systems [14–16], to mention the most common examples. In the samples poled by external dc voltage, an internal electric field can be formed due to redistribution of charges within the single layer [17,18] or multilayer structures [19,20]. The (1ω) EA spectroscopy can be used to study the electronic features at the interfaces, for example, the Schottky barrier height [5,6,21], the existence of insulating interfacial layer in the near-electrode region [22] or interface species at organic/organic heterojunction [23]. It has been reported that a molecular “Stark probe” sensitive to the local

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electric field was applied to measuring the field distribution across thin organic films [10]. Furthermore, average electric field distribution in operating multilayer organic devices like electroluminescent (EL) diodes [19,24,25] and photovoltaic (PV) cells [26] has been measured recently by EA technique. The knowledge of internal electric field is essential for understanding the physical mechanisms underlying the operation of these devices. In addition, it is important to know properties of internal electric fields built in the samples before drawing conclusions about charge separation mechanisms in organic photoconductors because quantum efficiency of charge generation is greatly affected by F_i , especially in the low-field regime [27].

In this work, we apply the electroabsorption spectroscopy to detect internal electric fields in vacuum-evaporated films of several organic compounds (for molecular structures see Fig. 1) which are commonly used in organic light-emitting diodes as hole-transporting materials (Fig. 1a) or fluorescent (Alq₃) and phosphorescent (PtOEP and Ir(ppy)₃) emitters (Fig. 1b). The measurements were made on the single layer sandwich structures, Al/organic film/Al/quartz, under ambient conditions. Despite two nominally the same Al electrodes used, the EA response on the fundamental frequency (ω) of the applied sinusoidal electric field has been detected. The analysis of the (1ω) EA

effect indicates a sample asymmetry and the presence of an internal electric field (F_i) in the cell. A comparison of (1ω) EA and (2ω) EA signals enabled to evaluate values of electric field strength, F_i . The possible origin of internal electric field is discussed.

2. Electroabsorption

An electric field (F) modulates the absorption spectrum of a chromophore molecule or an aggregate of molecules (with established orientation) via the Stark shift, $\Delta E(F)$, of the transition energy,

$$\Delta E(F) = -\Delta m \cdot F - \frac{1}{2} F \cdot \Delta p \cdot F, \quad (1)$$

where Δm is the change in the permanent dipole moment and Δp is the change in polarizability tensor accompanying ground state to excited state transition. The field-induced change of the absorption coefficient ($\Delta\alpha$) can be determined taking into account the band shift effect expressed by Eq. (1). In an ensemble of randomly oriented chromophores, the film average of $\Delta\alpha$ is proportional to the square of electric field strength (quadratic electrochromism) [1],

$$\Delta\alpha = B(E) \cdot F^2. \quad (2)$$

In Eq. (2), B stands for the function expressing the shape of electroabsorption spectrum and is proportional to the third-order dc Kerr nonlinear susceptibility $\chi^{(3)}$ [6]. In microscopic scale, B depends on molecular parameters Δm and Δp . The local electric field (F) which interacts with a molecule is assumed to be resultant of the applied sinusoidal field (F_e) and a static internal field (F_i) [3,11,15],

$$F = F_e \sin(\omega t) + F_i. \quad (3)$$

The permanent internal electric field F_i can arise due to inhomogeneities introduced to the system during the preparation procedure. As discussed in Section 1, the internal (built-in) field F_i may have several origins; all of them express asymmetry of the system. In Eq. (3), $F_e = fU_0/d$, where f is the local field correction factor and U_0 is the external voltage amplitude applied to the sample of thickness d . If the molecule is considered to reside in a dielectric medium forming a spherical cavity, then the correction factor can be expressed as $f_L = (\epsilon + 2)/3$ in the Lorentz approach to local electric field. For example, in one study using relative dielectric permittivity $\epsilon = 3$, we thus obtain $f_L \cong 1.7$. The electric field-induced change in the light intensity (I) passing through the sample,

$$\frac{\Delta I}{I} \cong -\Delta\alpha d, \quad (4)$$

can be expressed in terms of a Fourier series as

$$\frac{\Delta I}{I}(t) = A + \left(\frac{\Delta I}{I}\right)_{1\omega} \cdot \sin(\omega t) + \left(\frac{\Delta I}{I}\right)_{2\omega} \cdot \cos(2\omega t). \quad (5)$$

The measured rms values of the first $[(1\omega)$ EA] and second $[(2\omega)$ EA] harmonics of $\Delta I/I$ are given by

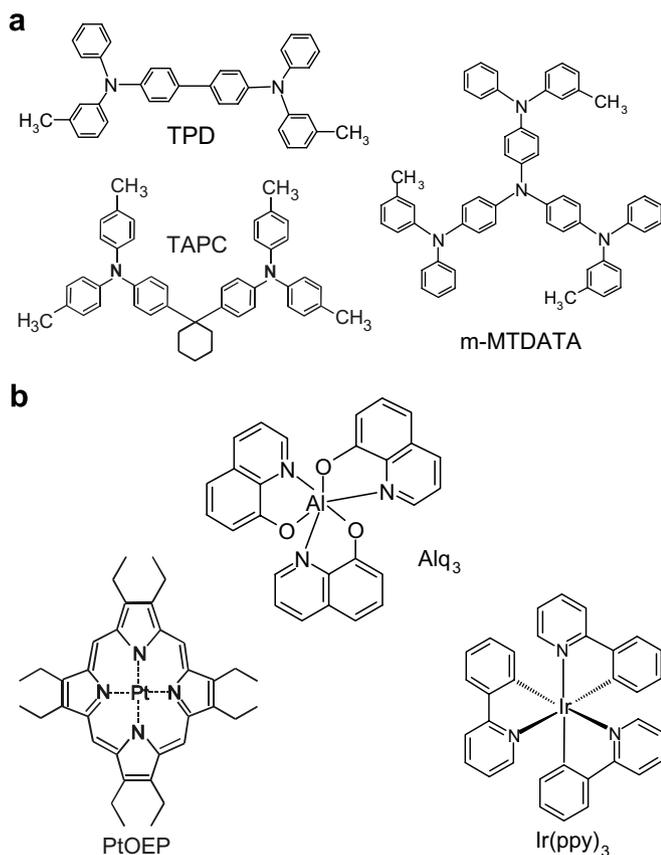


Fig. 1. The molecular structures of organic compounds under present investigation: (a) triphenylamine-based hole transporting materials (TPD, TAPC and *m*-MTDATA), (b) organic complexes: Alq₃, PtOEP and Ir(ppy)₃.

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