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Electroabsorption in vacuum-evaporated films of bathocuproine

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Abstract—Electric field-modulated absorption (EA) spectra were measured in vacuum evaporated films of bathocuproine (BCP), the phenanthroline derivative commonly used in organic light-emitting diodes. The EA spectra are interpreted in terms of the standard Stark spectroscopy analysis using a comparison of the EA spectrum with first and second absorption derivatives. The dipole moment and polarizability changes upon photoexcitation were calculated for the lowest energy singlet excited states in BCP films. The excited states are recognized as Frenkel excitons carrying intramolecular charge transfer (CT) character.

Bathocuproine (2, 9 - dimethyl - 4, 7 - diphenyl - 1, 10 - phenanthroline, BCP; see the inset of Fig. 1), is the electron-transporting material commonly used as a hole-blocker or blue emitter in organic light-emitting diodes (OLEDs) [1, 2]. In OLEDs the emissive layer is subjected to electric fields exceeding 10^6V/cm, therefore electric field modification of excited states is of importance. For example, under such a high electric field, intermolecular charge transfer (CT) process can be enhanced, resulting in the formation of separated electron-hole pairs. Consequently, the population of emitting states is reduced, as observed in electric field-induced photoluminescence quenching experiments [3]. The exciton quenching processes responsible for the observed high field drop in electroluminescence quantum efficiency of OLEDs are currently under extensive debate [1]. To gain insight into the electric field effect on the excitation process of electronic states in BCP, we report here an electroabsorption study of BCP vacuum-evaporated neat films.

Electroabsorption spectroscopy (Stark effect spectroscopy) is a straightforward way to infer the charge redistribution in excited molecular systems (for a review article see Ref. [4]). An electric field (**F**) changes usually the absorption spectrum of a molecule or an aggregate of molecules via the shift, $\Delta E(\mathbf{F})$, of the transition energy (E), due to the Stark effect,

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

where **Δm** is the change in the permanent dipole moment and **Δp** is the change in polarizability tensor accompanying the ground state to excited state transition.

The field-induced change ($\Delta\alpha$) of the absorption coefficient (α) can be expanded with respect to energy in a Mc Laurin series and truncated at the quadratic term. The average of $\Delta\alpha$ in an isotropic ensemble of molecules is given then by [5]

$$\Delta\alpha = \left(\frac{1}{2}\overline{\Delta p}\frac{\mathrm{d}\alpha}{\mathrm{d}E} + \frac{1}{6}(\Delta m)^2\frac{\mathrm{d}^2\alpha}{\mathrm{d}E^2}\right)F^2 = \mathrm{B}(E)\cdot F^2 \qquad (2)$$

Here, B stands for the function expressing the spectral dependence of $\Delta\alpha$. Equation (2) was derived, assuming a single non-degenerate electronic transition.

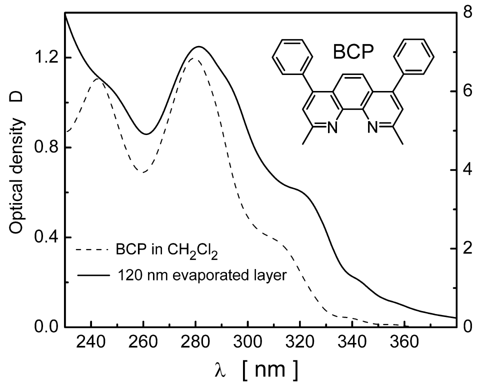

Fig. 1. Absorption spectrum of a 120 nm-thick BCP film (solid line) along with the absorption spectrum of BCP in CH_2Cl_2 (dashed line).

The decomposition of the electroabsorption spectrum ($\Delta\alpha$) into absorption derivative components allows to extract information on dipole moment (Δm) and average polarizability ($\overline{\Delta p}$) changes. An electroabsorption spectrum should reproduce the first derivative of the absorption spectrum ($\mathrm{d}\alpha/\mathrm{d}E$) if the polarizability term dominates and it should mimic the second derivative of the absorption spectrum ($\mathrm{d}^2\alpha/\mathrm{d}E^2$) if the permanent dipole moment is of importance. The more advanced methods of EA spectra analysis (not based on Eq. (2)) in organic solids, especially in polyacenes, have been developed by Petelenz and coworkers [6].

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The relative change of light intensity passing through the sample detected at a second harmonic (2ω) of applied sinusoidal voltage frequency (ω) can be expressed by

$$(2\omega)\,\mathrm{EA} \equiv \left(\frac{\Delta I}{I}\right)_{2\omega\,\mathrm{rms}} = \frac{1}{2\sqrt{2}}\,F_{\mathrm{e}}^{\,2}\cdot \mathrm{B}(E)\cdot d \qquad (3)$$

In Eq. (3), $F_{\mathrm{e}} = f\,U/d$, f is the local field correction factor and U is the external voltage amplitude applied to the sample of thickness d. The local field correction factor f can be expressed as $f = (\varepsilon+2)/3$ in the Lorentz approximation or as $f = 3\varepsilon/(2\varepsilon+1)$ in the Onsager approach, which for typical relative permittivity $\varepsilon = 3$ give the values of $f = 1.7$ (Lorentz) or $f = 1.3$ (Onsager).

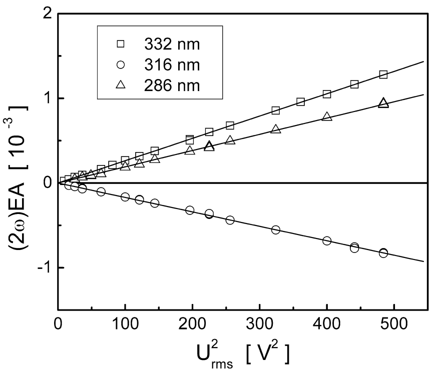

Fig. 2. The (2ω)EA signal versus the second power of rms voltage applied to the BCP sample (d = 120 nm) at various wavelengths of the absorbed light.

The BCP films were deposited by thermal evaporation in vacuum (~ 10^{-3}Pa) onto quartz substrates which were cleaned ultrasonically in an isopropanol bath prior to loading into a vacuum deposition chamber. The electro-absorption was measured using 100÷200-nm-thick films (controlled with a Tencor Alpha Step 500 Profiler) sandwiched between two semi-transparent Al electrodes applying a sinusoidal voltage, $U(t)=U_0\sin(\omega t)$. The (2ω)EA signal was recorded at the second harmonic of the fundamental voltage frequency (ω), employing a phase-sensitive technique. All spectra were monitored at constant optical resolution (60÷80cm^{-1}). Further details of experimental setup are described in our previous paper [7].

Ordinary absorption spectra were recorded with a Perkin-Elmer Lambda 10 spectrophotometer. A typical example is shown in Fig. 1, where a 120-nm-thick film absorption spectrum is compared with the absorption spectrum of BCP in a polar solvent (CH_2Cl_2). It is clearly seen that the absorption spectrum of the film displays all the features of the solution spectrum. Moreover, the rather small red shift (< 50meV) of the absorption spectrum of the film with respect to that of solution suggests that a matrix (solvent) shift arising from non-resonance interaction between an excited molecule and its ground state solid environment is insignificant. Therefore, we infer that the electronic states in BCP films are spatially well-localized within a molecular dimension and we design them as Frenkel excitons.

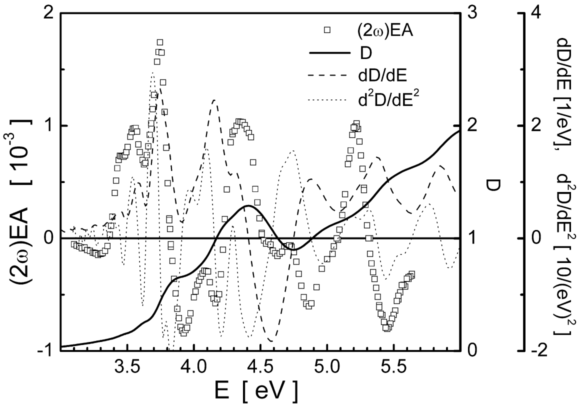

Fig. 3. The experimental (2ω)EA spectrum of a 120-nm-thick BCP film (squares) in comparison with the first derivative (D1, dashed line) and second derivative (D2, dotted line) of the ordinary absorption spectrum (D, solid line). The rms voltage U_{rms}=22V.

The (2ω)EA signals increase with the square of the applied voltage as predicted by the Stark effect-based equation (3), independent of the wavelength (Fig. 2). In Fig. 3 the spectrum of (2ω)EA signal is compared with the first (D1) and second (D2) derivatives of the optical density spectrum (D). The derivative spectra were computed by the Savitzky-Golay method including suitable smoothing procedures. In the low energy region the (2ω)EA signal follows the first derivative of the absorption spectrum (D1) with the scaling factor leading to the average polarizability change upon photoexcitation, $\overline{\Delta \mathrm{p}} \cong 40 \pm 10\,\text{Å}^3/f^2$ for this spectral range. In the Lorentz local field approximation (f=1.7), we get the value of $\overline{\Delta \mathrm{p}} \cong 14\,\text{Å}^3$, which is in agreement with those obtained for other small organic molecules [7, 8].

The higher energy part of EA spectrum in Fig. 3 is more complicated and cannot be analyzed by direct comparison with the global D1 and D2 spectra. Instead, the measured absorption spectrum was decomposed ($D = \sum_n D_{\mathrm{n}}$) into a number of Gaussian profiles D_{n} as displayed in Fig. 4.

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A reasonably good fit of the experimental (2ω)EA data with Eq. (4):

$$(2\omega)\mathrm{EA} = a\frac{\mathrm{d}D}{\mathrm{d}E} + \sum_{n=2}^{6} b_{\mathrm{n}} \frac{\mathrm{d}^2 D_{\mathrm{n}}}{\mathrm{d}E^2}, \qquad (4)$$

has been obtained, assuming an average polarizability change $\overline{\Delta p}=(21\pm5)Å^3/f^2$ throughout the whole spectrum range and Δμ varying for different electronic transitions (E_{n}) as given in the last column of Table 1. In the fitting of experimental data a non-linear least-squares procedure based on the Levenberg-Marquardt algorithm [9] was applied.

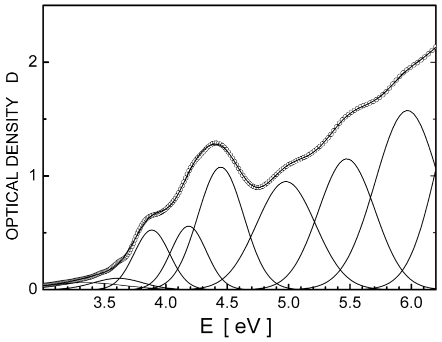

Fig. 4. The measured absorption spectrum of BCP film from Fig. 1 (circles), and its Gaussian profile analysis. The solid line obtained by the superposition of the Gaussian components.

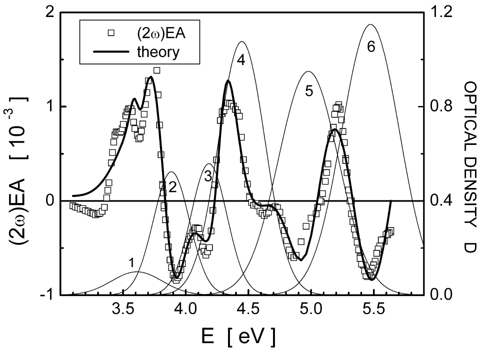

Fig. 5. The experimental (2ω)EA spectrum of the BCP film from Fig. 3 (squares) in comparison with the best fit of equation (4) (thick solid line) based on the first six Gaussian components (1 to 6) of the absorption spectrum from Fig. 4.

The energy positions of Gaussian bands correspond satisfactorily to the electronic transition energies calculated recently in reference [10], using time-dependent density functional theory (TD DFT with a B3LYP functional and 6-31G* basis set) as displayed in Table 1. According to Ref. [10], the low energy singlet electronic transitions in a BCP molecule are highly localized in the phenanthroline moiety and contain contributions of $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ primary transitions due to the effective spatial overlap between frontier molecular orbitals of n or π origin. We ascribe our relatively small values of Δμ=(2.4÷6.0)D/*f*, extracted from the EA experiments, to intramolecular charge redistribution taking place during photoexcitation. The intermolecular charge transfer in solid BCP seems to be rather improbable. The electron transfer between two nearest-neighbor BCP molecules separated by $R\cong7.8$Å (the average distance between molecules in a BCP crystal structure [11]) would lead to $\Delta\mu\cong37$D, the value an order of magnitude greater than that extracted from the EA experiment.

Table 1. Spectral features of BCP and its dipole moment changes upon excitation.

Band	Energy [eV] (this work)		Energy [eV] (from DFT calculations [10])	Dipole moment change Δμ [Debye] (this work)
	Abs	EA		
1	3.61	3.61	3.36	-
2	3.89	3.98	3.94	6.0/f
3	4.18	4.18	4.05	2.4/f
4	4.45	4.45	4.47	4.0/f
5	4.98	4.94	-	5.2/f
6	5.47	5.43	-	5.0/f
7	5.97	-	-	-

In summary, the electroabsorption in vacuum evaporated films of BCP can be rationalized in terms of the Stark effect and the low energy singlet excited states in solid BCP are recognized as Frenkel excitons endowed with an intramolecular CT character.

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