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Electroabsorption in triphenylamine-based hole-transporting materials for organic light-emitting diodes

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Abstract

Electric-field modulated absorption (EA) spectra have been studied in solid films of triphenylamine (TPA)-based compounds, commonly used as hole-transporting materials in organic light-emitting diodes. The electroabsorption spectra of triphenyldiamine derivatives (TPD and TAPC) and a starburst amine dendrimer m-MTDATA are compared with those of TPA which is the building block of the molecules. The EA results indicate that properties of excited states of m-MTDATA and TAPC can be qualitatively rationalized in the terms of exciton interaction between TPA constituents. The lowest energy electronic excitations of m-MTDATA dendrimer are strongly delocalized within the area of the whole molecule. In contrast to m-MTDATA and TAPC, the TPD behavior in the electric field shows individual features that can not be derived from the optical properties of TPA monomers alone. The influence of excited state degeneracy on EA spectra is discussed. The consistent qualitative interpretation of EA spectra for compounds under investigation has been reached assuming that the second derivative lineshapes of EA signal originate from degenerate (in TPA and m-MTDATA) and possible quasi-degenerate states (in TAPC and TPD).
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1. Introduction

Triphenylamine (TPA) based compounds (see Fig. 1 for molecular structures of some typical examples as TPD, TAPC and m-MTDATA) are commonly used as hole-transporting materials (HTM) in organic light-emitting devices (OLEDs) [1–3]. In addition, these materials can be applied as emitters in organic electroluminescent (EL) devices [1–6] and electron donor and hole-transporting materials in organic photovoltaic (PV) devices [2,3,7]. In both types of devices (EL and PV) the recombination of an electron and hole to form exciton or the reverse process, exciton dissociation into free charge carriers are processes critical for the operation of these devices and

strongly dependent on electric field. For example, the high electric field can enhance the exciton dissociation and in this way reduce significantly EL quantum yield of OLEDs [1]. Recently, the effect has been studied employing electric field-induced photoluminescence quenching observed in triphenyldiamine derivatives (TPD and TAPC [8]) and starburst amines (m-MTDATA and 1-TNATA [9]). The more efficient exciton dissociation observed in TDATA-type starburst amines in comparison to that effect in TPD-type diamines has been attributed to a high degree of energy and charge delocalization over distances comparable with molecular dimensions of starburst amines [9]. The key point is to understand the nature of the excited states in this type compounds and determine all factors underlying various relaxation pathways of electronic energy including the radiative decay. Understanding the relationship between molecular or intermolecular structure and electronic or

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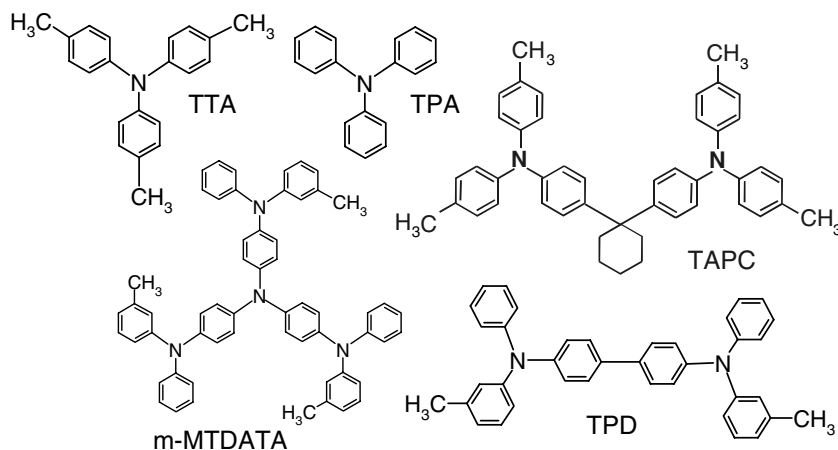 *E-mail address:* waldek@mif.pg.gda.pl (W. Stampor).

Fig. 1. The structures of molecules under present investigation.

optoelectronic properties of a material is essential for providing guidelines for device design with optimized performance parameters. A great experimental and theoretical research effort is currently being made in this field [10–13].

Electroabsorption (EA) spectroscopy (Stark effect spectroscopy) is a straightforward way to infer the charge redistribution accompanying electronic excitations in molecular systems (for a recent review see [14]). Upon application of an external electric field to sample the absorption spectrum is broadened, shifted and changed in intensity due to changes in permanent dipole moment (Δm), polarizability (Δp), and oscillator strength. Their contribution to the overall electro-optic effect can be extracted by comparing the observed electroabsorption spectrum with the derivatives of the ordinary absorption spectrum of the molecular system studied. The EA method has been recently applied to characterize and assign excited states in a series of emitters widely used in organic EL devices: poly(p-phenylene vinylene) (PPV) and its derivatives [15–17], 8-hydroxyquinoline aluminum (III) complex (Alq$_3$) [18], 2-phenylpyridine iridium (III) complex (Ir(ppy)$_3$) [19], Pt(II)octaethylporphyrin (PtOEP) [20] to mention a few examples. In particular, applying EA spectroscopy charge localization on individual quinolate ligands in the lowest excited states of solid Alq$_3$ [18] and charge delocalization on three phenylpyridine ligands in metal-to-ligand charge transfer (MLCT) states of Ir(ppy)$_3$ [19] predicted by quantum-mechanical calculations were satisfactorily confirmed.

In this EA study we investigate a charge redistribution upon excitation of solid triphenylamine based compounds (m-MTDATA, TAPC and TPD) and compare the properties of the whole molecule and those of its constituent TPA moieties. The EA results indicate that properties of excited states of m-MTDATA and TAPC can be qualitatively explained in the terms of exciton interaction between TPA segments. However, the EA spectra of TPD molecule show individual features that differ from what can be expected on the basis of this model.

2. Electroabsorption

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 Stark effect,

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

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. If the field-induced change ($\Delta \alpha$) of the absorption coefficient (α) is sufficiently small, it can be expanded with respect to energy in a Mc Laurin series and truncated at the quadratic term. In the case where the measured values of $\Delta \alpha(E,F)$ can be approximated by an averaged shift $\langle \Delta E \rangle$ and averaged broadening $\langle (\Delta E)^2 \rangle$ of an absorption band in an isotropic ensemble of molecules

$$\langle \Delta E \rangle = -\frac{1}{2}\overline{\Delta p}F^2, \tag{2}$$

$$\left\langle (\Delta E)^2 \right\rangle = \frac{1}{3}(\Delta m)^2 F^2, \tag{3}$$

the average of $\Delta \alpha$ is given by [21]

$$\Delta \alpha = \left(\frac{1}{2}\overline{\Delta p}\frac{d\alpha}{dE} + \frac{1}{6}(\Delta m)^2 \frac{d^2\alpha}{dE^2}\right)F^2 = B(E) \cdot F^2 \tag{4}$$

Here, B stands for the function expressing the spectral dependence of $\Delta \alpha$. Eq. (4) was derived assuming a single non-degenerate electronic transition. Decomposition of the electroabsorption spectrum ($\Delta \alpha$) into absorption derivative components allows to extract information on dipole moment (Δm) and polarizability ($\overline{\Delta p}$) changes. The essential characteristics of excited states can often be obtained from a direct comparison of the lineshape of EA spectrum and the dominant derivative term in Eq. (4). An electroabsorption spectrum should reproduce the first derivative of the absorption spectrum ($d\alpha/dE$) if the polarizability term dominates (see Fig. 2a for schematic illustration of the effect) and it should mimic the second