Chemical Physics 352 (2008) 48–56

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Linear and nonlinear optical spectroscopic characterisation of triphenylamine and 1,2,3-tris(3-methylphenylphenylamino)benzene

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ARTICLE INFO

Article history:
Received 4 March 2008
Accepted 16 May 2008
Available online 22 May 2008

Keywords:
Triphenylamine TPA
Tris(3-methylphenylphenylamino)benzene
m-MTDAB
OLED hole-transport materials
Neat films
Absorption spectroscopy
Fluorescence spectroscopy
Reverse saturable absorption
Attenuation/amplification of spontaneous emission
Excited-state absorption

ABSTRACT

The molecule triphenylamine (TPA) in tetrahydrofuran (THF) and the starburst triphenylamine oligomer 1,3,5-tris(3-methylphenylphenylamino)benzene (m-MTDAB) in THF and as neat film are characterized. Absorption and emission spectroscopic parameters are determined. The S_0–S_1 transition is found to be weak ($n\pi^*$ transition) with small fluorescence quantum yield and efficient non-radiative decay (singlet–triplet intersystem crossing). The S_0–S_1 absorption cross-section spectra in the tails of the broad first absorption bands of the compounds are separated out by radiative lifetime determination and applying the mirror-image relation between absorption and emission. Excimer formation is observed for m-MTDAB neat films, its photo-dynamics is studied, and monomer and excimer stimulated emission cross-section spectra are extracted. Reverse saturable absorption is observed for TPA and m-MTDAB in picosecond laser nonlinear transmission measurements (laser duration 35 ps, laser wavelength 347.15 nm) and the responsible excited-state absorption cross-sections are determined. A new method is developed to calculate the excited-state absorption cross-section spectra of the samples in the fluorescence spectral region by amplification/attenuation of spontaneous emission measurements. The excited-state absorption is found to be larger than the stimulated emission for TPA in THF and for m-MTDAB films excluding their lasing ability. For m-MTDAB in THF the stimulated emission is found to be slightly larger than the excited-state absorption at the wavelength position of peak fluorescence emission.

1. Introduction

The molecule triphenylamine (TPA) and derivatives thereof are applied as hole-transport materials in electrophotography [1,2], and in organic light emitting diodes [3–5]. They are used in the backbone [6–10] or in side-groups [10–13] of polymers applied in light emitting diodes. The triphenylamine dimers TPD (also called tetraphenylbenzidine TPB) [14], 3-methyl-TPD [15], and 4-methyl-TPD [16] are laser active materials both in liquid solution and as neat films. Laser action was also achieved on triphenylamine based conjugated polymers [17] and triphenylamine dimer based conjugated and non-conjugated polymers [18].

Star-shaped oligomers and dendrimeric structures of triphenylamines are attractive photo- and electro-active organic materials because of their amorphous nature [10,19–21]. Methyl-substituted derivatives of the starburst molecule, 1,3,5-tris(diphenylamino)benzene (TDAB) belong to low-molecular-mass organic materials which form stable amorphous glasses with glass transition temperatures above room temperature [22–24]. 1,3,5-Tris(3-methylphenylphenylamino)benzene (m-MTDAB) has stable amorphous glass properties below 49 °C, it crystallizes at about 88 °C, and melts at 183 °C [24]. Its synthesis is described in [22,23]. It is used as hole-transport material in light emitting devices [25].

Here TPA dissolved in THF and m-MTDAB dissolved in THF and as neat thin film are characterized towards their lasing ability/disability by linear and nonlinear absorption spectroscopy as well as spectral and temporal emission studies. Absorption cross-section spectra, stimulated emission cross-section spectra, fluorescence quantum distributions, fluorescence quantum yields, degrees of fluorescence polarisation, and fluorescence lifetimes are determined. The fluorescence spectra of m-MTDAB revealed excimer formation. Therefore the photo-dynamics of excimer formation in m-MTDAB films is analysed. A quantitative fluorescence analysis for TPA and m-MTDAB revealed small S_1–S_0 stimulated emission cross-section spectra. The corresponding S_0–S_1 absorption cross-section spectra of TPA and m-MTDAB hidden in the broad first absorption bands of the compounds are extracted applying the Einstein relation between absorption and stimulated emission. Since excited-state absorption at the pump laser wavelength lowers the efficiency of lasing, this parameter was determined for the studied samples by nonlinear transmission measurement of the pump laser (second harmonic of picosecond ruby laser, wavelength 347.15 nm). A decrease in transmission with rising pump pulse intensity is found (reverse saturable absorption). For the lasing ability of a material it is required that the stimulated emission

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doi:10.1016/j.chemphys.2008.05.006

cross-section is larger than the excited-state absorption cross-section. The stimulated emission cross-section spectrum is extracted from the fluorescence spectra, the fluorescence quantum yields and the fluorescence lifetimes. For the determination of the excited-state absorption cross-section spectra of samples in the fluorescence spectral region a new method of pump pulse energy density dependent measurement of amplification or attenuation of spontaneous emission is developed.

2. Experimental

TPA was bought from Aldrich Company. m-MTDAB was bought from American Dye Source, Inc., Quebec, Canada (product name: ADS04HTM). The structural formulae of TPA and m-MTDAB are shown in Fig. 1 and some physical parameters are given there. All experiments have been carried out at room temperature under ambient conditions.

m-MTDAB was studied both dissolved in THF and as neat film. TPA was only studied dissolved in THF since no good films could be made by spin-coating because of crystallisation. Thin films of m-MTDAB were prepared by spin-coating from THF solution on glass substrates.

The optical constants (refractive index spectrum, $n(\lambda)$, and absorption coefficient spectrum, $\alpha(\lambda)$) and the film thickness, d_f, of a m-MTDAB neat film were determined by reflectance, $R(\lambda)$, and transmittance, $T(\lambda)$, measurements as described previously [26,27].

The absorption cross-section spectra, $\sigma_{a,s}(\lambda)$, of TPA and m-MTDAB in THF were measured with a commercial spectrophotometer (Cary 50 from Varian). The absorption cross-section spectrum, $\sigma_{a,f}(\lambda)$, of a m-MTDAB neat film was determined by using the spectral shape of the neat film absorption coefficient spectrum, $\alpha_f(\lambda)$, and assuming equal absorption cross-section integrals for the film and the liquid solution in the displayed wavelength range [28]. The relation $\sigma_{a,f}(\lambda) = \alpha_f(\lambda) \int \sigma_{a,s}(\tilde{\nu})\,d\tilde{\nu} / \int \alpha_f(\tilde{\nu})\,d\tilde{\nu}$ is used where $\tilde{\nu} = \lambda^{-1}$ is the wavenumber. The molecule number density in the thin film is given by $N_f = \alpha_f/\sigma_{a,f}$.

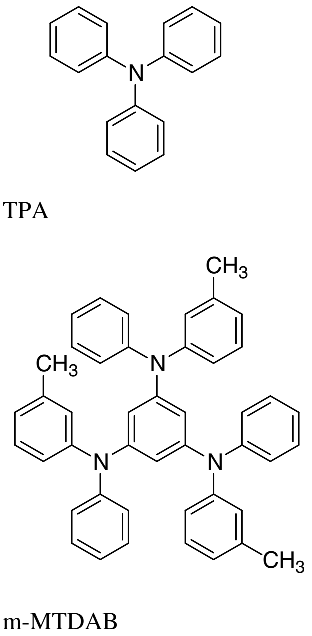

Fig. 1. Structural formulae of triphenylamine (TPA, sum formula: $C_{18}H_{15}N$, molar mass: 245.32 g mol^{-1}, density: 0.774 g cm^{-3}, melting point 127 °C, boiling point: 347.5 °C) and of 1,3,5-tris(3-methylphenylphenylamino)benzene (m-MTDAB, sum formula: $C_{45}H_{39}N_3$, molar mass: 621.83 g mol^{-1}, glass transition temperature: 49 °C, melting point: 183 °C).

The fluorescence analysis of TPA and m-MTDAB in THF and of a m-MTDAB thin film was carried out with a self-assembled fluorimeter [29]. The data analysis is described in [30]. The dye quinine sulphate dihydrate (from Aldrich) in 1 normal aqueous H_2SO_4 solution (fluorescence quantum yield, $\phi_{F,R}(C) = 0.546/(1 + 14.5C)$ at 25 °C where C is the concentration in mol dm^{-3} [31]) was used as reference standard. The degree of fluorescence polarization, $P_F(\lambda) = [S_{F,\parallel}(\lambda) - S_{F,\perp}(\lambda)]/[S_{F,\parallel}(\lambda) + S_{F,\perp}(\lambda)]$, was determined by vertically polarized excitation and detection of the fluorescence signal polarized parallel $(S_{F,\parallel})$ and perpendicular $(S_{F,\perp})$ to the excitation light.

Temporal fluorescence traces of the samples were measured by dye excitation with second harmonic pulses of an active and passive mode-locked ruby laser [32] (pulse duration 35 ps, wavelength 347.15 nm) and detection of the fluorescence signal with a fast micro-channel-plate photomultiplier (Hamamatsu type R1564U-01) in connection with a fast real-time digital oscilloscope (LeCroy type 9362).

The saturable absorption or reverse saturable absorption behaviour [33] of TPA and m-MTDAB in THF at 347.15 nm was studied by excitation-intensity dependent energy-transmission measurement of picosecond second harmonic ruby laser pulses through a cell of 1 mm thickness. From the intensity dependent transmission the responsible excited-state absorption cross-section is extracted below by numerical simulation.

Light emission from TPA/THF and m-MTDAB/THF solutions is studied by transverse pumping the compounds in a quartz glass cell of 1 cm width and 1 mm thickness. The solutions are excited with pulses of our frequency doubled mode-locked ruby laser. The beam profile of the excitation pulses was shaped to a line focus of 14.5 mm width (FWHM) and 0.245 mm height (FWHM) using crossed defocusing and focusing cylindrical lenses. The emitted signal along the line-focusing direction is collimated and directed to a spectrometer – diode-array detection system (observation of spectral amplification or attenuation). A scheme of the experimental arrangement is shown in the insert of Fig. 11b.

The wave-guided edge emission of a m-MTDAB neat film on a glass substrate was studied by transverse pumping the film in a similar arrangement as used for the cell amplification/attenuation experiments. The plate surface was tilted 7° off the perpendicular direction towards the excitation beam direction in order to better collect the light propagating along the film substrate interface [34].

3. Results

3.1. Linear optical spectroscopic characterization

The transmittance spectrum and the reflectance spectrum of a m-MTDAB thin film on a fused silica substrate are shown in Fig. 2. The film was prepared by spin-coating of m-MTDAB in THF at a concentration of 10 mg/ml with an angular speed of 450 rpm. The absorption coefficient spectrum and the refractive index spectrum together with the film thickness are extracted by a Fresnel equation approach [26,27]. The obtained spectra are shown in Fig. 3. The film thickness turned out to be $d_f = 52$ nm. The absorption maximum occurs slightly below 316 nm (limit of experimental measurement range). At 316 nm the light penetration depth is $d_p = \alpha_f^{-1} = 52.5$ nm. The refractive index spectrum shows the expected dispersion shape. In the displayed wavelength range the film refractive index is larger than the fused silica or optical glass refractive index. Therefore optical wave-guiding takes place in films above a critical film thickness [35]. For transverse electric modes (TE modes, electrical field vector in plane of the film) this minimum film thickness is [35]