

Influence of peripheral substituents on the optical properties of heterocyclic azo dyes



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ABSTRACT

Optical properties, such as the real and imaginary parts of the dielectric function and the optical energy band gap, of new heterocyclic azo dyes thin films were investigated using spectroscopic ellipsometry combined with transmittance measurements. The topography of studied compounds was also examined by atomic force microscopy.

It was found that the optical properties of the azo dyes materials strongly depend on the type of substitution in the azobenzene moiety, namely leads to a change in the value of refractive index, as well as bathochromic shifts of the absorption structure.

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1. Introduction

Azobenzene is an aromatic molecule where two phenyl rings are bridged by an azo ($-\text{N}=\text{N}-$) linkage. The extended conjugation gives rise to strong absorption at ultraviolet (UV) and visible (VIS) wavelengths. The spectral and photo-physical properties of the azobenzene are highly sensitive to its substitution pattern.

One of more essential trademarks of this compound is the fact that the azobenzene appears in two forms, and has the ability for reversible photoisomerization between a thermally stable *trans*-state and a metastable *cis*-state upon the absorption of a photon. The isomerization reaction produces structural changes in the azobenzene configuration and significantly affects its spectroscopic and physical properties; this is the key to the unique optical and photomechanical effects observed in azobenzene-containing material systems.

Azobenzenes are interesting because they combine the properties of anisotropy with photoresponsive behavior, and this can give rise to applications in areas such as liquid crystal (LC) displays, nonlinear optical devices, information storage devices, surface-relief holography and optical switching [1–10].

The investigated azo dyes were embedded into a poly (methyl methacrylate) (PMMA) polymer matrix. Azobenzene-

PMMA systems are known as optical materials with large nonlinearities.

In this paper we present the optical properties (e.g. the real and imaginary parts of the dielectric function as well as the optical energy band gap) of thin films of azobenzene derivatives measured using spectroscopic ellipsometry (SE) combined with transmittance measurements (T). Atomic force microscopy (AFM) was used to examine the topology of the studied thin films.

The aim of this work was to show how the introducing of different substituents into azo dyes leads to a change in their optical properties. These chemical modifications allow the optical properties of heterocyclic azo dyes to be varied throughout the UV–VIS–NIR spectral range.

2. Experimental

2.1. Materials Synthesis

¹H NMR (400 MHz) spectra were recorded on a Mercury (Varian) 400 spectrometer with tetramethylsilane as internal standard.

4-Aryl-5-aryl(hetaryl)diazanyl-1,3-thiazol-2-amines were obtained similar to a described procedure [11]. The preparation methods of the related derivatives are shown in the reaction scheme, which is presented in Fig. 1.

4-(4-Bromophenyl)-5-(phenyldiazanyl)-1,3-thiazol-2-amine (A2): Orange solid, yield 75%. ¹H NMR (400 MHz, DMSO-d₆):

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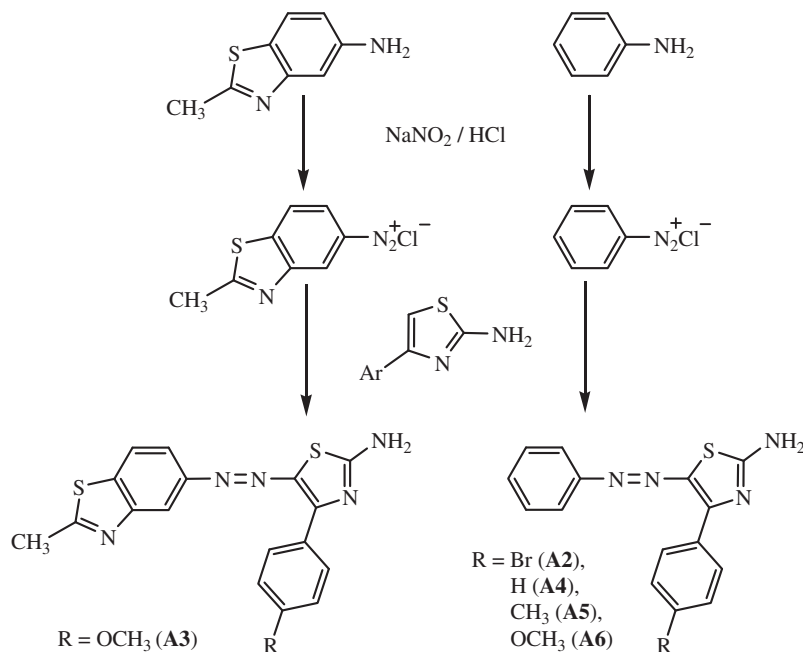


Fig. 1. Synthesis route and chemical structures of the heterocyclic azo dyes.

$\delta = 7.38$ (t, $J = 6.8$ Hz, 1H, Ph), 7.49 (t, $J = 6.8$ Hz, 2H, Ph), 7.66 (d, $J = 6.8$ Hz, 2H, Ph), 7.73 (d, $J = 8.0$ Hz, 2H, Ar), 8.16 (d, $J = 8.0$ Hz, 2H, Ar), 8.44 (br. s, 2H, NH₂) ppm.

4-(4-Methoxyphenyl)-5-[(2-methyl-1,3-benzothiazol-5-yl)diazenyl]-1,3-thiazol-2-amine (A3): Dark red crystals, yield 80%. ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 2.83$ (s, 3H, CH₃), 3.88 (s, 3H, OCH₃), 7.01 (d, $J = 8$ Hz, 2H, Ar), 7.75 (d, $J = 7.2$ Hz, 1H, Het), 7.88 (d, $J = 7.2$ Hz, 1H, Het), 8.13 (s, 1H, Het), 8.25 (d, $J = 8$ Hz, 2H, Ar), 8.49 (br. s, 2H, NH₂) ppm.

4-Phenyl-5-(phenyldiazenyl)-1,3-thiazol-2-amine (A4): Dark red crystals, yield 84%. ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 7.30$ (t, $J = 7.6$ Hz, 1H), 7.40–7.47 (m, 5H), 7.63 (d, $J = 7.6$ Hz, 2H), 8.14 (d, $J = 7.2$ Hz, 2H), 8.42 (br. s, 2H, NH₂) ppm.

4-(4-Methylphenyl)-5-(phenyldiazenyl)-1,3-thiazol-2-amine (A5): Red solid, yield: 89%. ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 2.41$ (s, 3H, CH₃), 7.25–7.30 (m, 3H, Ph), 7.42 (t, $J = 7.2$ Hz, 2H, Ph), 7.62 (d, $J = 7.6$ Hz, 2H, Ar), 8.13 (d, $J = 7.6$ Hz, 2H, Ar), 8.43 (br. s, 2H, NH₂) ppm.

4-(4-Methoxyphenyl)-5-(phenyldiazenyl)-1,3-thiazol-2-amine (A6): Red solid residue, yield: 88%. ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 3.87$ (s, 3H, OCH₃), 6.99 (d, $J = 7.2$ Hz, 2H, Ar), 7.28 (t, $J = 6.8$ Hz, 1H, Ph), 7.41 (t, $J = 6.8$ Hz, 2H, Ph), 7.62 (d, $J = 6.8$ Hz, 2H, Ph), 8.23 (d, $J = 7.2$ Hz, 2H, Ar), 8.46 (br. s, 2H, NH₂) ppm.

2.2. Preparation of thin films

The glass substrates used were carefully cleaned in a commercial surfactant using ultrasonication. A spin-coating technique was used to make thin films of poly(methyl methacrylate) (PMMA) matrices doped with the A2–A6 heterocyclic azo dyes with controlled thickness.

The solution of 1,2,2-trichloroethane containing PMMA 100 g/L and azobenzene (A2–A6) 10% wt. from PMMA coated on glass slides. The principle of deposition is based on a homogeneous spreading out of the solution on the rotating substrate with an angular speed of 1000 rpm and a spin duration of 60 s. Immediately after the deposition the thin films were cured in an 60 °C oven for 60 min in order to eliminate any remaining solvent.

2.3. Measurements

Atomic force microscope (AFM) (Innova device from Bruker) was used to examine the topology of the studied thin films. The imaging scan size was 1 $\mu\text{m} \times 1 \mu\text{m}$; standard Si tips were used.

Ellipsometric azimuths (Ψ and Δ) were measured for three angles of incidence: 65°, 70° and 75°. The complex dielectric function and thickness of the azo-containing films were determined using spectroscopic ellipsometry (V-VASE ellipsometer from J.A. Woolam Co., Inc.) combined with transmittance measurements (made using a Cary 5000 from Agilent) in the photon energy range from 4.5 eV to 0.6 eV (275–2000 nm).

2.3.1. Ellipsometry method

The change of the polarization state of reflected light from a sample surface is measured in the ellipsometry technique. The reflecting properties of an isotropic sample are expressed as the ratio of the complex Fresnel coefficients \tilde{r}_p and \tilde{r}_s for light which is polarized parallel and perpendicular to the plane of incidence, respectively. The ellipsometric quantities Ψ and Δ are defined by the well-known fundamental equation [12]:

$$\tilde{\rho} = \frac{\tilde{r}_p}{\tilde{r}_s} = \tan \Psi e^{i\Delta} \quad (1)$$

where $\tan \Psi$ measures the ratio of the amplitudes of the electric field components and Δ measures the relative phase change.

Spectroscopic ellipsometry is a standard optical technique for determining the macroscopic linear optical response of thin films represented by the complex dielectric function:

$$\tilde{\epsilon} = \epsilon_1 + i\epsilon_2 = \tilde{n}^2 \quad (2)$$

where $\epsilon_1 = n^2 - \kappa^2$ and $\epsilon_2 = 2n\kappa$ are the real and imaginary parts of dielectric function, respectively, and $\tilde{n} = n + i\kappa$ is complex refractive index. The extinction coefficient (κ) is proportional to the absorption coefficient (α):

$$\kappa = \frac{\alpha\lambda}{4\pi} \quad (3)$$

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