

Application and spectral characterization of vapour deposited 4-aminoazobenzene dyes nanosized films

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In this paper two types of 4-aminoazobenzene derivatives were vapour deposited and investigated as nanosized films. The films were characterized by UV-VIS spectroscopy. Birefringence was induced in the films by pump lasers with wavelengths of 355 nm and 444 nm within the absorbance band of the azo chromophores used. Laser light at 635 nm was used to probe the photoinduced birefringence. The recording dynamics and temperature dependence of birefringence have been presented. It was found that 4-aminoazobenzene derivative nanosized films have good photoanisotropic properties for optoelectronic device application.

Keywords: Vapour deposition, 4-aminoazobenzene derivatives, Azo dyes, Thin films, Photoinduced birefringence.

INTRODUCTION

Azobenzene dyes undergo *trans*→*cis* photoisomerization by laser irradiation with an appropriate wavelength. The reverse *cis*→*trans* isomerization can be driven by light or occurs thermally in the dark. Azobenzene's photochromatic properties make it an ideal component of numerous molecular devices and functional materials [1]. According to the spectral properties, nature and position of the substituents in the aromatic rings azobenzene derivatives can be classified (by Rau) [2] as: (i) azobenzene derivatives (ABn); (ii) aminoazobenzene derivatives (aAB); (iii) pseudostilbenes (pSB). The pseudostilbenes "push-pull" azo dyes are good chromophores for photoinduced birefringence with blue or green laser pump. The photoinduced birefringence is due to reorientation of azobenzene molecules perpendicular to the polarization of the recording light [3]. It is defined as $\Delta n = n_{\perp} - n_{\parallel}$, where n_{\perp} is the component of the refractive index

perpendicular to the polarization of the recording beam, and n_{\parallel} is the component parallel to it. Therefore the illumination in UV-VIS region where the π → π^* absorbs is an efficient process for photoinduced orientation [4]. The substituents influence isomerization of azobenzenes by steric and electronic effects. The presence of electron withdrawing (EW) groups like -COOH, -CHO, -CN, -NO₂ decrease the energy of the electron transitions, where the π → π^* and n → π^* bands are well separated. The electron donating (ED) substituents lead to unsymmetrical electron distribution (push-pull) and effectively conjugation with lower resonance energy compared to the unsubstituted azobenzenes [1, 4]. Smart surface design on photoisomerizable materials has attracted much attention because of potential applications as optical photoswitches, reversible information storage, organic solar cells, bioengineering devices, nonlinear optic materials, polyelectrolyte multilayers, liquid crystals and other photoactive and photomechanical devices [5, 6]. Therefore in this paper we have investigated two "push-pull" azobenzenes dyes (Azo-a and Azo-d) for optical data storage by photoinduced birefringence with

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laser pump at $\lambda = 355$ and 444 nm as vapour deposited nanosized films. The electron transitions spectra were calculated by TD-DFT/ B3LYP functional combined with the standard 6-31+G(d,p) basis set in vacuo in order to predict the excitation energies and comparison with experimental results.

EXPERIMENTAL

Vapour deposition of nanosized films

The thin films of azo dyes were prepared by evaporation from Knudsen type vessels on quartz substrates. The temperature of evaporation was kept between 45 - 60°C . Temperature of substrate was 15°C , controlled by thermal regulator with Peltier element. Sample thickness was 230 nm for Azo-a and 70 nm for Azo-d. They are measured by high-precision Talystep profilometer with 10 nm accuracy. Samples were evaporated on substrates of glass and melted quartz.

Spectral characterization

The UV-VIS spectra were recorded on a Cary 5E (Varian) spectrophotometer in the 250 - 800 nm range as nanosized films on quartz substrates.

Birefringence measurement

The birefringence (Δn) was determined by measuring the Stokes parameters of probe laser beam ($\lambda_{\text{probe}} = 635$ nm, power < 2 mW) passing through the samples. The measurement was performed by PAX5710 Polarimeter (Thorlabs) and Δn is calculated from the Eq. 1 [7, 8]:

$$\Delta n = \frac{\lambda_{\text{probe}}}{2\pi d} \arctan\left(\frac{S_3}{S_2}\right) \quad (1)$$

where d is the film thickness, and S_2 and S_3 are two of the four Stokes parameters. Birefringence is induced independently by two diode pumped solid state (DPSS) lasers: (i) an UV laser with wavelength $\lambda_{\text{rec1}} = 355$ nm and power 20 mW, and (ii) a visible blue laser with $\lambda_{\text{rec2}} = 444$ nm and power 35 mW. The thermal erasure was studied using heating stage THMS600 (Linkam Scientific) with temperature stability $< 0.1^\circ\text{C}$. Rate of heating was set to $1^\circ\text{C}/\text{min}$.

Quantum chemical calculations

The optimization of molecular geometry and excitation states of the studied molecules were performed by GAUSSIAN 09W software package using Time-Dependent Density-Functional Theory TD-DFT/ B3LYP functional combined with the standard 6-31+G(d,p) basis set in vacuo [9].

RESULTS AND DISCUSSION

Fig. 1 presents calculated and experimental electronic (UV-VIS) spectra of vapour deposited nanosized films of Azo-a and Azo-d. The electron transitions $\pi \rightarrow \pi^*$ ($S_0 \rightarrow S_2$) $\lambda_{\text{max}} = 376$ and 328 nm and $n \rightarrow \pi^*$ ($S_0 \rightarrow S_1$) $\lambda_{\text{max}} = 461$ nm bands of Azo-a is separated due to the unsymmetrical electron distributions (push-pull) of two EW $-\text{NO}_2$ groups at positions $2'$ and $4'$, while in the spectra of Azo-d they are overlapped in a broad peak at $\lambda_{\text{max}} = 351$ nm because of properties of the ED groups: $-\text{CH}_3$ (+I effect) at position $2'$ and $-\text{Br}$ ($-I$ and $+M$ effects) at position $4'$. The calculated spectrum of Azo-a is in a good agreement with experimentally obtained from nanosized film data, while for Azo-d the experimental λ_{max} was shifted 57 nm higher in the energy scale compared to the computed spectrum. Quantum mechanics determines the properties of nanomaterials with one dimension in the range 1 to 100 nm, and calculation methods to deal with nanomaterials are being developed. When one or more dimensions of a material fall below 100 nm, especially below 20 nm, dramatic changes in the optical, electronic, chemical, and other properties from those of the bulk material can occur. The reason is behavior of the materials close to the properties of single molecule in vacuo.

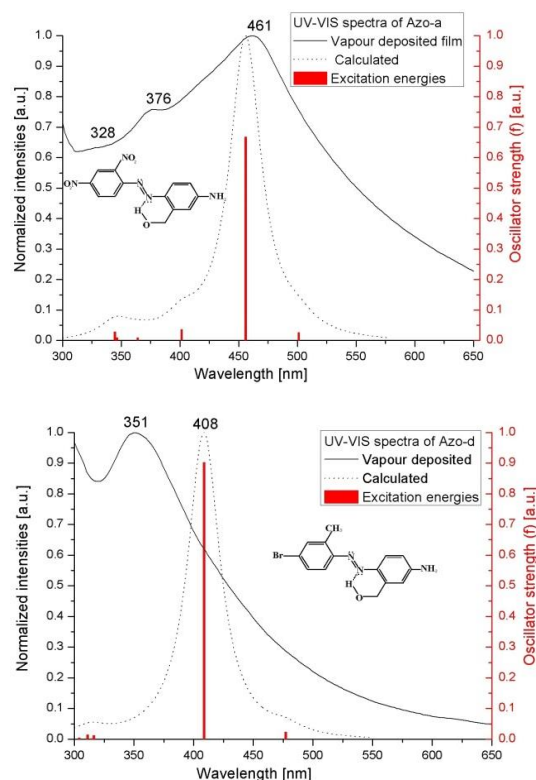


Fig. 1. UV-VIS spectra of Azo-a and Azo-d as vapour deposited nanosized films and theoretically calculated by TD-DFT/ B3LYP 6-31+G(d,p) level of theory in vacuo.

The UV-VIS spectra of azo dyes have determined the further investigation of photoinduced birefringence with laser pump at $\lambda = 355$ and 444 nm for potential application in optical storage devices or diffractive optical elements with unique polarization properties [7]. Fig. 2 presents the data from the birefringence measurement of Azo-d. During the first 60 sec only the probe beam is on allowing to determine the measurement baseline. Then the recording laser is started and increase of the birefringence is observed. Its maximal value is $\Delta n_{\max} = 0,006$ for $\lambda_{\text{rec}1} = 355$ nm, and $\Delta n_{\max} = 0,01$ for $\lambda_{\text{rec}2} = 444$ nm. After 300 sec from the beginning of experiment the recording laser is stopped. There is an initial decrease of the birefringence, but then it reaches a stable state with more than 70% of the anisotropy retained in the film. This indicates good stability and possibility to use these azo dyes for various applications.

The temperature dependence of the birefringence is shown in Fig. 3. The values plotted are normalized to the birefringence value measured for the starting temperature of 26°C .

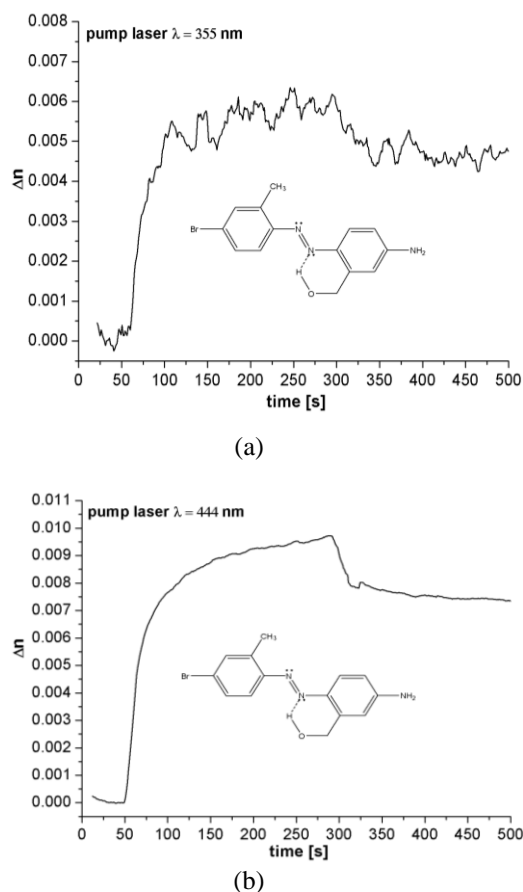


Fig. 2. Time dependence of the photoinduced birefringence Δn in Azo-d in case of recording with pump lasers with wavelengths: (a) 355 nm, and (b) 444 nm, respectively.

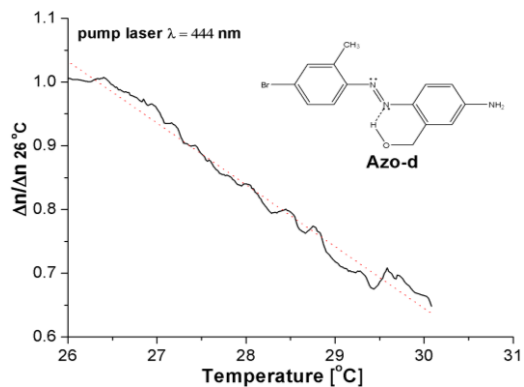


Fig. 3. Temperature dependence of the birefringence in Azo-d. Birefringence is recorded on illumination at 444 nm

CONCLUSIONS

Two “push-pull” azo dyes (Azo-a and Azo-d) were vapour deposited as nanosized thin films. The experimental UV-VIS spectra were compared with the theoretically calculated ones. It was found that the calculated spectrum of Azo-a is in a good agreement with the experimentally measured data, while for Azo-d the experimental λ_{\max} value was shifted 57 nm higher in the energy scale compared to the computed spectrum. When the layer is less than 100 nm thick the properties of the film are more close to the properties of single molecule. The observed 57 nm shifting most probably is a result of the impact of Br atom and the interaction of molecules with each other. Vapour deposited nanosized film of Azo-d was investigated by optical birefringence for a potential application as optical storage material. It has been found after pump laser wavelengths at $\lambda = 444$ nm and 355 nm the stable state with more than 70% of the anisotropy is retained in the film.

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REFERENCES

1. H. Bandara and S. Burdette, *Chem. Soc. Rev.*, **41**, 1809 (2012).
2. H. Rau, in: *Photoreactive Organic Thin Films*, (eds.) Zhao, Y. & Ikeda, T. Elsevier Sci. Ltd, 2002, p. 3-48.
3. T. Todorov, L. Nikolova, N. Tomova, *Appl. Opt.*, **23**, 4309 (1984).

4. A. Natansohn, P. Rochon, *Chem. Rev.*, **102**, 4139 (2002).
5. K. Yager and C. Barrett, Azobenzene Polymers For Photonic Applications, (eds.) Yue Zhao and Tomiki Ikeda, Book chapter in Smart Light-Responsive Materials, John Wiley & Sons Inc., 2009, p. 1-27.
6. L. Zhan, J. Cole, *Appl. Mater. & Interfaces*, **6**, 3742 (2014).
7. L. Nedelchev, A. Matharu, S. Hvilsted, P. S. Ramanujam, *Appl. Opt.*, **42**, 5918 (2003).
8. L. Nikolova, P. S. Ramanujam, Polarization Holography, Cambridge Univ. Press, Cambridge, 2009.
9. M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. Hratchian, A. Izmaylov, J. Bloino, G. Zheng, J. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. Peralta, F. Ogliaro, M. Bearpark, J. Heyd, E. Brothers, K. Kudin, V. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. Burant, S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. Millam, M. Klene, J. Knox, J. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. Stratmann, O. Yazyev, A. Austin, R. Cammi, C. Pomelli, J. Ochterski, R. Martin, K. Morokuma, V. Zakrzewski, G. Voth, P. Salvador, J. Dannenberg, S. Dapprich, A. Daniels, O. Farkas, J. Foresman, J. Ortiz, J. Cioslowski, and D. Fox, Gaussian, Inc., Wallingford CT, 2009.

ПРИЛОЖЕНИЕ И СПЕКТРАЛНО ХАРАКТЕРИЗИРАНЕ НА ОТЛОЖЕНИ 4-АМИНОАЗОБЕНЗЕН БАГРИЛА В НАНОРАЗМЕРНИ ФИЛМИ

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(Резюме)

В статията са изследвани два вида вакуумно отложени 4-аминоазобензенови производни като наноразмерни филми. Филмите са изследвани с UV-VIS спектроскопия. Оптично индуцираното двулъчепречупване е изследвано чрез пробен лазер с дължина на вълната 635 nm. Изследването е направено чрез възбуждане с напompващи лазери с дължини на вълните 355 nm и 444 nm от абсорбционните спектри на азобагрилата. Изследвани са зависимостите от времето и температурата на двулъчепречупването на азохромофорите. Установено е, че 4-аминоазобензеновите производни като наноразмерни филми притежават добри фотоанизотропни свойства за приложение в оптоелектронни устройства.