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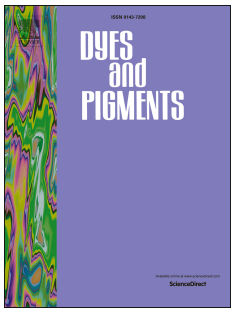

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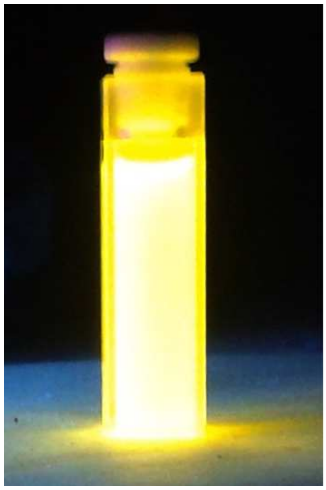

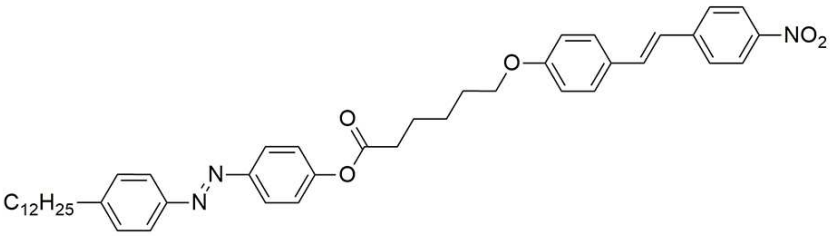

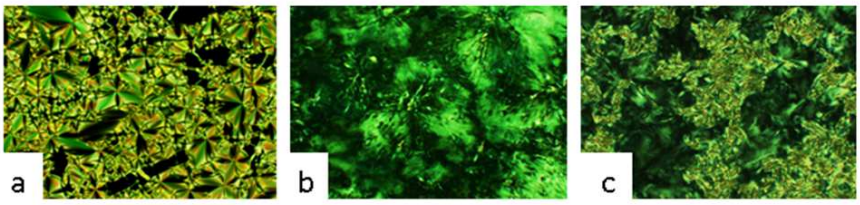

Novel fluorescent liquid crystal containing azobenzene and stilbene moieties- synthesis, mesogenic and spectroscopic studies

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Abstract

This paper presents synthesis and characterization of new rigid core dye composed of two chromophore moieties such as azobenzene and stilbene parts. During this study liquid-crystalline properties was investigated and found as expected. An additional and unforeseen phenomenon of solid state polymorphism was also noticed. Furthermore, fluorescent properties were examined and confirmed by the fluorescence spectroscopy. This initial study gave very interesting and promising results which can be basis for further studies of such new type of azo-stilbene based substances.

Keywords: liquid crystals, azobenzene, stilbene, fluorescence, smectic, dye

1. Introduction

Liquid crystals containing azo moiety are extensively studied group of compounds. Main reason of this situation are their interesting physicochemical as well as optical properties. An important role in the azobenzene derivatives studies plays the photosensitivity [1], which enables the *trans-cis-trans* isomerization of -N=N- group. Such compounds can be used as molecular switches [2], where the UV light causes the transition from trans to cis isomer. Whereas light from visible range causes back transition. Highly developed optoelectronic industry is looking for such type of materials, with a number of specific properties for example luminescent. In order to achieve this property a special group must be implemented to the molecule structure. For this purpose, commonly used are f-electron elements such as europium [3] or lanthanum [4,5]. In recent years, heterocyclic components such those based on oxidazole [6] or coupled ring systems like perylenes became increasingly popular [7].

Main aim of this study was design and optimization of the synthesis root of rod-like molecule with two dye groups: azobenzene and stilbene. Such fusion should provide very interesting properties such as liquid-crystallinity, fluorescent properties and also very interesting but probably complicated *trans-cis* isomerization in both photosensitive moieties. Some of these attributes were investigated and are presented in this communication.

2. Material and method

2.1. Measurements Setup

Elemental analysis measurements were conducted by the use of Vario EL III elemental analyzer and the NMR spectra were measured by the use of Bruker Avance III 500 MHz high resolution spectrometer. As solvent deuterated chloroform was used.

Liquid-crystalline mesophases were investigated by three different methods. Characteristic textures were observed by the use of polarized optical microscopy (POM) and phase transitions temperatures were detected by thermo-optical analysis (TOA). Enthalpies of phase transitions were measured by the use of differential scanning calorimetry (DSC). All calorimetric measurements were made using Perkin Elmer 8500 calorimeter with scan rate 10 K min^{-1}. During the microscopic observations Olympus polarized light microscope BX61-P (TRF) with Linkam heating stage and Bresser camera 9 MPix were used. Absorption spectra were obtained using the UV-Visible spectrophotometer (Varian Cary500 instrument), while the emission spectra were recorded on a Hitachi F4500 Fluorescence Spectrofluorometer with an excitation wavelength of 365 nm (mercurial lamp with filter). Scan rate of 1 nm/s. All measurements were carried out in dichloromethane.

2.2. Synthesis

All starting materials like 4-dodecylaniline, 4-hydroxybenzaldehyde, 4-nitrophenylacetic acid and all other simple inorganic and organic substances were purchased and used without additional purification. Detailed synthesis procedures from Figure 1 are available in appendix.

Full synthesis scheme is shown in Figure 1. This project involves synthesis of azo and stilbene part simultaneously. Moreover, as a spacer between chromophores 6-bromohexanoic acid to azobenzene part from final molecule was introduced. Synthesis of compound (1) was done according to the procedure described in [8], whereas compound (3) according to the modified procedure, which is available in [9]. Compound (2) was obtained by the esterification reaction of (1) and the above mentioned 6-bromohexanoic acid in the presence of DCC (N,N'-Dicyclohexylcarbodiimide) and DMAP (4-Dimethylaminopyridine). The last step of presented scheme is combination of (2) and (3) in etherification process, in which the final product (4) is formed. ^{1}H NMR and elemental analysis data of final product and intermediates are available in appendix.

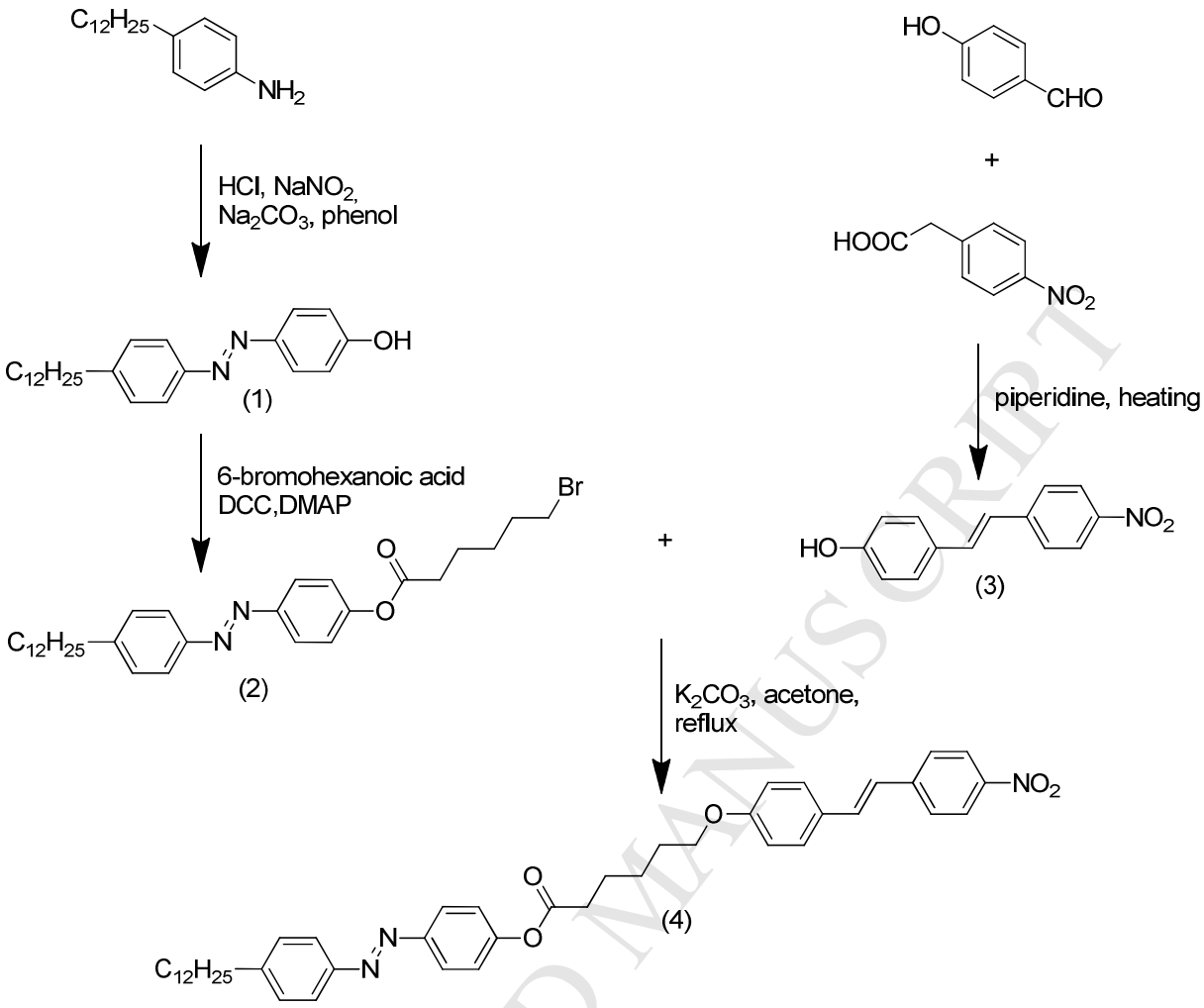

Figure 1. Full synthesis scheme of new azobenzene-stilbene dye.

3. Results and Discussion

Synthesized material (4) was designed based on rigid geometry of the molecule, which is well-known for the formation of liquid-crystalline phases. Studies of mesogenic properties were started with microscopic observations (POM), which confirmed the presence of one mesophase - smectic A (Figure 2a) and were continued by the use of thermo-optical analysis (TOA) and differential scanning microscopy (DSC). Surprisingly, observed mesophase exists in very wide temperature-range (about 80°C). Detailed data from the above-mentioned experiments are available in appendix. During cooling cycle in POM measurements two

crystalline forms with different textures were observed (Figure 2b and 2c). The occurrence of two crystalline phases were also confirmed by DSC measurements.

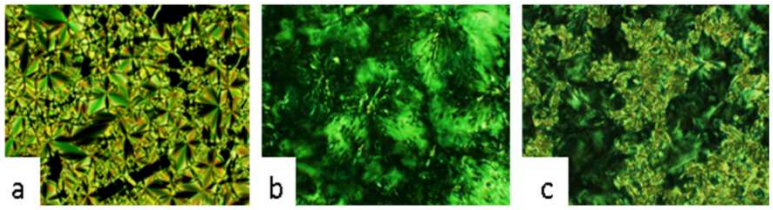

Figure 2. Textures observed during POM measurements captured in cooling cycle: a) focal-conic texture of liquid-crystalline smectic A observed at 172 °C b) first crystalline form (CrI) observed at 108°C. Moreover, rising of second crystalline form (CrII) is slightly visible c) two crystalline forms at 85°C: CrI- dark area of the picture, CrII- bright area.

Design of presented material involved the introduction of stilbene part to the chemical structure. Stilbenes are well-known in the literature due to their fluorescent properties. Therefore, obtained compound (4) was checked if it is able to emit some light. According to the absorption and emission spectra, which were done in dichloromethane solution (available in appendix), (4) absorbs light in the UV range (λ_{Amax}=350 nm) and emits visible light (λ_{Emax}=550 nm). This very important feature strongly enlarges potential application capabilities of presented material. This experiment shows that trough the combination two different dyes we are able to obtain much more interesting material, which combines best features of applied moieties.

4. Conclusion

In this study one new dye with two chromophore groups (azo and ethane double bond) was successfully synthesized and its basic features such as: mesogenic and luminescent properties were proved. It was discovered that the compound is still sensitive to the light from both the UV and visible range (azobenzene part), but also exhibits luminescence in the visible

area (stilbene part). Furthermore, the rigid shape of the molecule provides liquid-crystalline properties (smectic A). According to the obtained results we suppose that presented dye possess very promising application capabilities and can be used for further more detailed studies.

5. Acknowledgements

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- New dye with two chromophore groups was designed and synthetized
- The optimized synthesis root is presented
- Novel dye has interesting properties of both intermediates
- Short characterization of mesogenic and fluorescent properties is showed