



Rigidified merocyanine dyes with different aspect ratios: Dichroism and photostability



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ABSTRACT

A series of new rigidified merocyanines were investigated with regard to their optical properties as dichroic dyes. Guest/host-mixtures of the dyes were prepared using a liquid crystal and a reactive mesogen mixture. Their dichroism was studied using linearly-polarized UV/Vis-spectroscopy. A strong dependence of the dichroic ratio on the aspect ratio, the number of double bonds in the molecular structure, and on the maximum wavelength of absorption was found. A strategy to increase the aspect ratio has also been demonstrated. Additionally, the photostability was characterized using continued irradiation with polychromatic light from a xenon source. High photostability was found in all host mixtures in the absence of oxygen by alignment in a matrix. The suitability for their application as dichroic dyes in thin layer polarizers and guest/host-displays is herein discussed.

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1. Introduction

Currently, thin-film-transistor liquid crystal displays (TFT-LCDs) are the most popular flat panel displays due to their low weight, low power consumption and compact size [1]. An essential part of TFT-LCDs is the polarizing film, which is generated by stretching a polymer film containing iodine and/or dichroic dye molecules [2]. Polyvinyl alcohol/iodine polarizing films are the most widely used examples of these due to their excellent optical properties with distinct and intense absorption in the UV/Vis region [3]. However, important limitations of these polarizing films are their high sensitivity towards humidity and towards elevated temperatures due to the sublimation of iodine [4–6].

Presently, these deficiencies are circumvented by a special lamination of the polarizing film but this packaging increases the overall thickness to several hundred microns, which makes its incorporation into the stack of functional layers within the display unfeasible. Instead, the polarizing film is typically applied on top of the display glass despite the occurrence of cross-talk by parallax

that restrict fill-factor and resolution. Therefore, so-called in-cell polarizers of less than 5 microns thickness are widely investigated for a possible integration into the LC display. A promising approach based on the seminal work by Broer utilizes dichroic guest/host polarizers [7]. He reported in 1989 that selective absorption of light could be achieved by aligning a dichroic dye (guest) in an oriented, polymerisable liquid crystalline host. The low viscosity of the reactive monomeric liquid crystal facilitates good alignment, while the *in situ* photopolymerization enables the selection of the optimum phase with highest molecular order [8]. This technology has been applied in the preparation of numerous optical devices, for example patterned retarders [9], broadband circular polarizers [10], wide viewing angle films [11], and cholesteric color filters [12]. Most important properties for an application as polarizing film are a high dichroic ratio and polarizing efficiency. Both properties can be improved by increasing the molecular order of the polymeric host or preceding mesophase and by increasing the aspect ratio of the dichroic dye for a better alignment in the anisotropic host matrix. We believe the latter approach is more promising because the use of higher ordered matrices usually requires a change from nematic to smectic mesophases but the reliable fabrication of good quality smectic layers is technically much more challenging [13].

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Also, new dichroic dyes have many other potential applications such as in guest/host displays. They were invented in the late 1960s, first based on the Heilmeyer/Zanoni mode [14] and later on the White/Taylor mode [15]. The latter mode does not require additional polarizers, which promises the fabrication of simpler device geometries with lower power consumption. The lack of effective dichroic dyes and the success of devices based on the twisted nematic mode halted the development of guest/host displays, but renewed interest is currently fueled by their comparatively low cost. Potential applications include large area information displays [16], reflective [17–19] and fluorescent displays [20], as well as windows and tinted goggles with adjustable transparency [21].

All these applications rely on the availability of dichroic dyes with appropriate properties. Most dichroic dyes that have been studied in displays are based on azobenzene and anthraquinone derivatives [22,23] and the objective of the work presented here is to evaluate the performance of merocyanine dyes as an alternative dichroic dye. Surprisingly few studies on the dichroism of merocyanines have been reported [13] although they have been tested for many other applications, such as in NLO devices [24], dye sensitized solar cells [25,26], medical peptide sensors [27], and water analysis [28], because of their strong and sharp absorption bands [29], pronounced fluorescence, solvatochromism and photochromism, and propensity to form aggregates [30,31].

Presented herein is the first study on the dichroism of rigidified merocyanine dyes, which have a rod-like shape of adjustable aspect ratio, adjustable linear optical properties [32], and are expected to possess high photostability. The merocyanine dyes investigated here consist of three cyanoacetates which bear different chromophoric units (trimethine **MC 1**, pentamethine **MC 2**, heptamethine **MC 3**), three cyanoacetates with tethered *p*-alkoxybenzoate units differing in their alkyl chain length (hexyl **MC 4a**, decyl **MC 4b** and tetradecyl **MC 4c**), and two other heptamethine derivatives (malononitrile **MC 5**, barbiturate **MC 6**), which carry strong acceptor groups and vary significantly in their aspect ratio (Scheme 1). To improve general solubility of the investigated compounds a benzoate unit was added to the alkyl chain in the case of derivative **MC 4**. Reported are the photostabilities of these dyes and the dichroic ratios of their mixtures with a liquid crystal (LC) and a reactive

mesogen mixture (RMM) as host matrices to assess their suitability for applications in thin film polarizers. Also presented is an analysis of how different aspect ratios of the merocyanine dyes correlate with the observed dichroic ratios.

2. Experimental

2.1. Materials

2.1.1. Synthesis

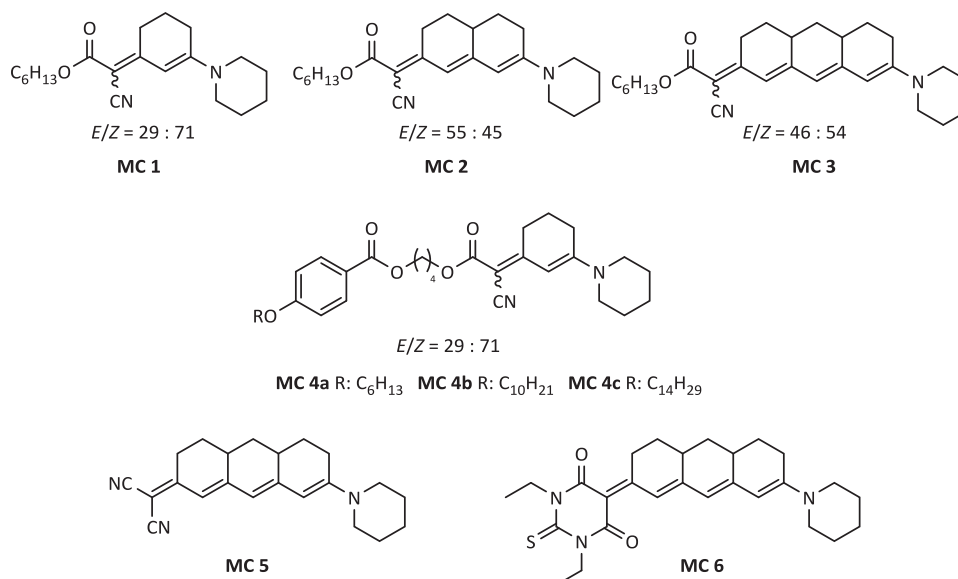
All commercial reagents were used without further purification. Solvents were dried and distilled under nitrogen prior to use and all reactions were carried out under a nitrogen atmosphere with Schlenk-type glassware. Flash chromatography was performed on silica gel, grain size 40–63 μm (Fluka).

2.1.2. Guest/host cells

As a LC host-material the LC-Mixture M677 of Nematel was used (a mixture of cyano- and alkoxy phenylcyclohexyl-, biphenylcyclohexyl- and bicyclohexylphenyl-derivatives). The clearing point of this mixture is 115 $^{\circ}\text{C}$. As reactive mesogen mixtures (RMM) were used RMM14 ($T_{\text{cl}} = 154^{\circ}\text{C}$) and RMM34 (70 $^{\circ}\text{C}$) of Merck KGaA and a 1:1 mixture of RMM34 and ST01011 (153 $^{\circ}\text{C}$) of the Synthron GmbH.

2.2. Characterization

The following instruments were used for characterization of the compounds. NMR: Bruker Avance 500 (^1H , 500 MHz; ^{13}C , 125 MHz). ^1H and ^{13}C NMR spectra were referenced to TMS (Me_4Si $\delta_{\text{H}} = 0.0$ ppm, $\delta_{\text{C}} = 0.0$ ppm) as an internal standard. The following abbreviations were used: s (singlet), d (doublet), t (triplet), m (multiplet), m_{c} (centered multiplet). All spectra were recorded at room temperature. Chemical shift calculations and 2D experiments (COSY and HMBC) supported the assignments of the signals. IR: Bruker Vector 22 FT-IR Spectrometer with MKII golden gate single reflection Diamant ATR system. To describe the intensities following abbreviations were used: vs (very strong), s (strong), m (medium), w (weak). Elemental analyses: Carlo Erba Strumentazione Elemental Analyzer, Model 1106. HRMS (ESI): Bruker



Scheme 1.

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