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Dielectric spectroscopy analysis of molecular reorientation in dye doped nematic liquid crystals having different preliminary orientation

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Abstract

Reorientation tendencies of liquid crystal (LC) molecules are investigated for two different fundamental orientation configurations that are known as homogenous (HG) and homeotropic (HT). A hybrid LC content, including red and blue dyes together, is employed in these two cells enabling measurements in different spectral regions by two different lasers. Influence of preliminary orientation on the behaviors of molecules under dark and illuminated circumstances is extracted from the performed measurements. Dielectric anisotropy is also studied for the mentioned conditions and its dependency is quantitatively estimated by capacitive measurements.

Keywords: Liquid crystals; Dye doped; Dielectric anisotropy

1. Introduction

LC are highly nonlinear optical materials due to their susceptible property activating under even relatively low optical fields. Several nonlinear mechanisms investigated so far have revealed the promising characters of these materials. The difference in refractive indices, for fields polarized along, and perpendicular to, the director axis brings about a large birefringence property from visible to infrared spectral regime [1]. Because of the large broadband birefringence of nematic LC, it is obvious that these highly sensitive films could be applied in a variety of image processing systems operating with low optical power.

It is also experimentally proved that doping a small amount of dye decreases the required threshold of molecular reorientation further in LC materials [2]. Since many dyes exist that will cover the entire visible spectrum, such dye doped nematic films are highly promising candidates for application as very broadband optical modulators and limiters, and other adaptive optics and coherent wave-mixing devices. Reorientation based effects causing the change of refractive index and observations of several interesting dynamic and storage wave-mixing effects have been studied extensively so far [3–6]. This phenomenon has potential applications such as holographic data storage. Compared with others, LC based systems require lower characteristic voltages to be applied for the realization of molecular response as well as relatively lower light power for efficient modulation of refractive index. Whatever the application is, the preparation of the sample is critical and there are two main preliminary orientation possibilities having mutual benefits. Effect of preliminary orientation, imposed by the surface pattern of the cell substrates, on the molecular reorientation mechanism is of primary importance in the design of LC devices. In the scope of this work, the so called Dielectric Spectroscopy Technique (DST) was applied for analyzing the dependency of

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molecular reorientation on common parameters of the subject such as preliminary orientation, order of laser pumping, applied voltage etc.

2. Method and experiment

There are various works concentrating on the electro-optical characterization of LC [7–10]. DST is a powerful technique successfully applied for understanding the molecular details and effect based tendencies of the investigated case [11]. Dielectric anisotropy, $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are parallel and perpendicular components of the electric permittivity, respectively, is estimated from capacitance measurements by eliminating dielectric permittivity of medium, ε, from Eq. (1).

$$C = \varepsilon_0 \varepsilon \frac{A}{d} \tag{1}$$

Here C is the capacitance value, ε_0 and ε are dielectric permittivity values of free space and concerned medium, respectively, A is the plate area and d is the thickness of the cell. By using capacitance values, dielectric constants were calculated according to Eq. (1) from where ε is eliminated.

Two samples were prepared both of which were filled with a hybrid composition made up of a nematic host E7 and two dyes that are Methyl red, 0.5% weight/weight and Disperse Blue 14, 0.5% weight/weight. One of the samples is HG, in which overall orientation of molecules is parallel to substrate surfaces, and the other one is HT, in which overall orientation is perpendicular to substrate surfaces. The schematic representation of molecular orientation of dyes and nematic host in HG and HT cells is shown in Fig. 1. Chemical formulae of the samples' components are depicted in Fig. 2. Due to the absorbance nature of our hybrid sample, Fig. 3, it was possible to use two different lasers alternatively; He–Ne (632.8 nm) and He–Cd (441.6 nm). The wavelengths of these lasers correspond to absorbance peaks of the devised sample and alternative usage of two different wavelengths in the experiment provided to demonstrate the exploitation of solely-absorbance originated effects on a single sample by two different pumping sources.

During the measurements incoming laser beam was arranged to cover the whole surface of the sample cell by a diverging lens and opaque masking permitted to precisely illuminate only the filled portion, which is roughly at the order of 0.25 cm^2. Thickness of the cells is $\sim$8.7 μm and Indium Tin Oxide (ITO) coated substrates enabled to apply voltage to samples. Experimental set-up is shown in Fig. 4. Impedance/gain phase

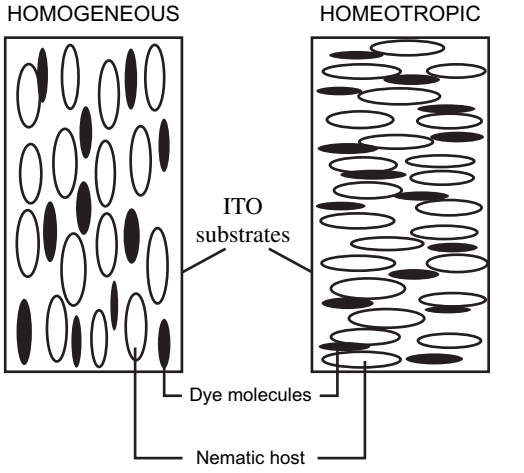

Fig. 1. The schematic representation of molecular orientation of dyes and nematic host in HG and HT cells.

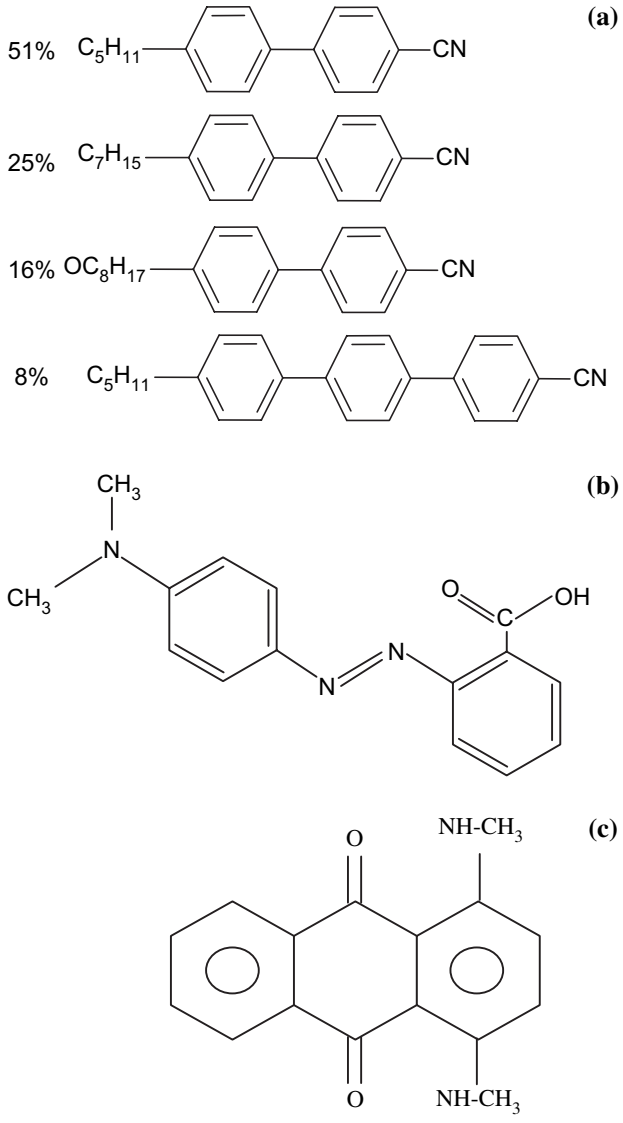

Fig. 2. Chemical components of the devised hybrid sample. (a) Nematic host E7, (b) Red dye (Methyl red), (c) Blue dye (Disperse Blue 14).

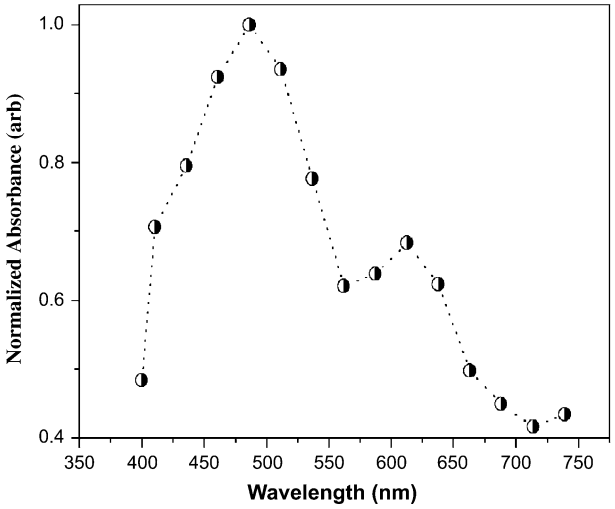

Fig. 3. Absorbance spectrum of the hybrid sample.

analyzer, (HP 4194 A) was used and various excitation voltages were examined. The time lag between successive measurements was arranged to be at the order of 10 s so that relaxation of LC molecules are satisfied after the laser is off and all measurements were performed at room temperature. We also have extracted dielectric anisotropy values as well as some other key electrical parameters and their dependencies on related conditions, for two different preliminary orientations.

3. Results and discussion

Molecular orientation of LC molecules determine the electro-optical behavior of the system and because laser molecule interaction causes molecules to reorient in these systems, our intention was to examine electro-optical measurements so that we could demonstrate the molecular reorientation based changes in capacitance, impedance and conductivity properties.

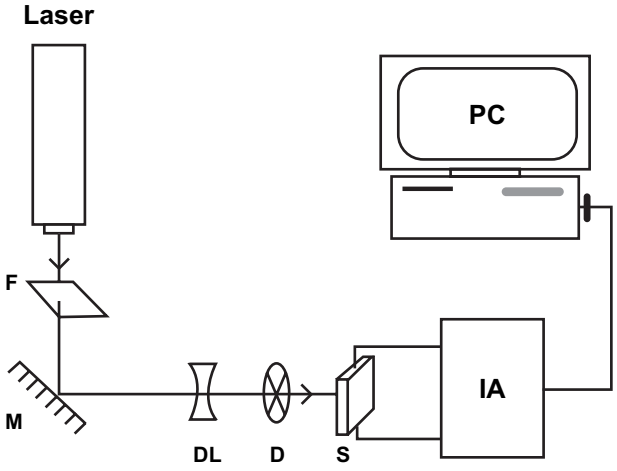

Fig. 4. Experimental set-up for DST analysis (F: filter; M: mirror; DL: diverging lens; D: diaphragm; S: sample; IA: impedance analyzer).

Fig. 5 depicts the dependency of impedance on applied voltage for dark and laser illuminated conditions. Because the applied electric field is parallel to the molecules in HT alignment, obtained impedance values are lower in comparison to HG where molecules are perpendicular to applied electric field. In the case of HG orientation, Fig. 5a, laser pumping causes shift of switching voltage in constructive trend while relatively low values of impedance peaks are obtained in HT orientation, Fig. 5b. These peaks are decreased by laser effect in this case at lower voltage values. Also, HG configuration has a broader band width with respect to HT and laser pumping causes this band width to be narrower as one can notice in Fig. 5. This is because it takes some potential interval for molecules to be parallel to applied electric field in case of HG alignment while the molecules are already parallel to field in HT. In fact, laser pumping helps this process in HG and required potential interval gets shorter with laser pumping. In the case of HG alignment, polarization of the optical field is at right angle to the molecular orientation at low voltage values that is why laser illumination does not affect the value of impedance while in HT orientation, parallel molecule–field orientation causes an increase in the photoconductivity whereby a decrease in impedance value is observed, Fig. 5b. In addition, He–Cd laser has more effect in HG cell since the absorbance of the sample is more in the corresponding wavelength, Fig. 3.

Due to the anisotropic property of LC, capacitance is dependent on external effects and our study demonstrates its dependency on voltage for a molecularly reorientable system. Related graphs are presented in Fig. 6. As it can be seen, molecules are in their original orientation when there is no voltage for relatively low frequencies (up to 1 MHz), i.e., minimum capacitance case, and once the voltage is applied reorientation starts, i.e., the situation at the beginning of voltage application. After a while, saturation happens, i.e., maximum capacitance case. After 1 MHz, the trend is changed dramatically in both HG and HT orientation with a decrease in the capacitance value depending on voltage. This is because the frequency rise alters the structure type from positive to negative. Regarding the dielectric constant, there are two structure types. One is called as positive dielectric anisotropy (p-type) and its dielectric constant along the director axis is larger than that along the axes perpendicular to the director and $\Delta\varepsilon$ is greater than zero in this case. The other type is called as negative dielectric anisotropy (n-type) and its dielectric constant along the director axis is smaller than that along the axes perpendicular to the director, $\Delta\varepsilon$ is less than zero [12,13]. Dependency of dielectric anisotropy on the frequency modulation is investigated in

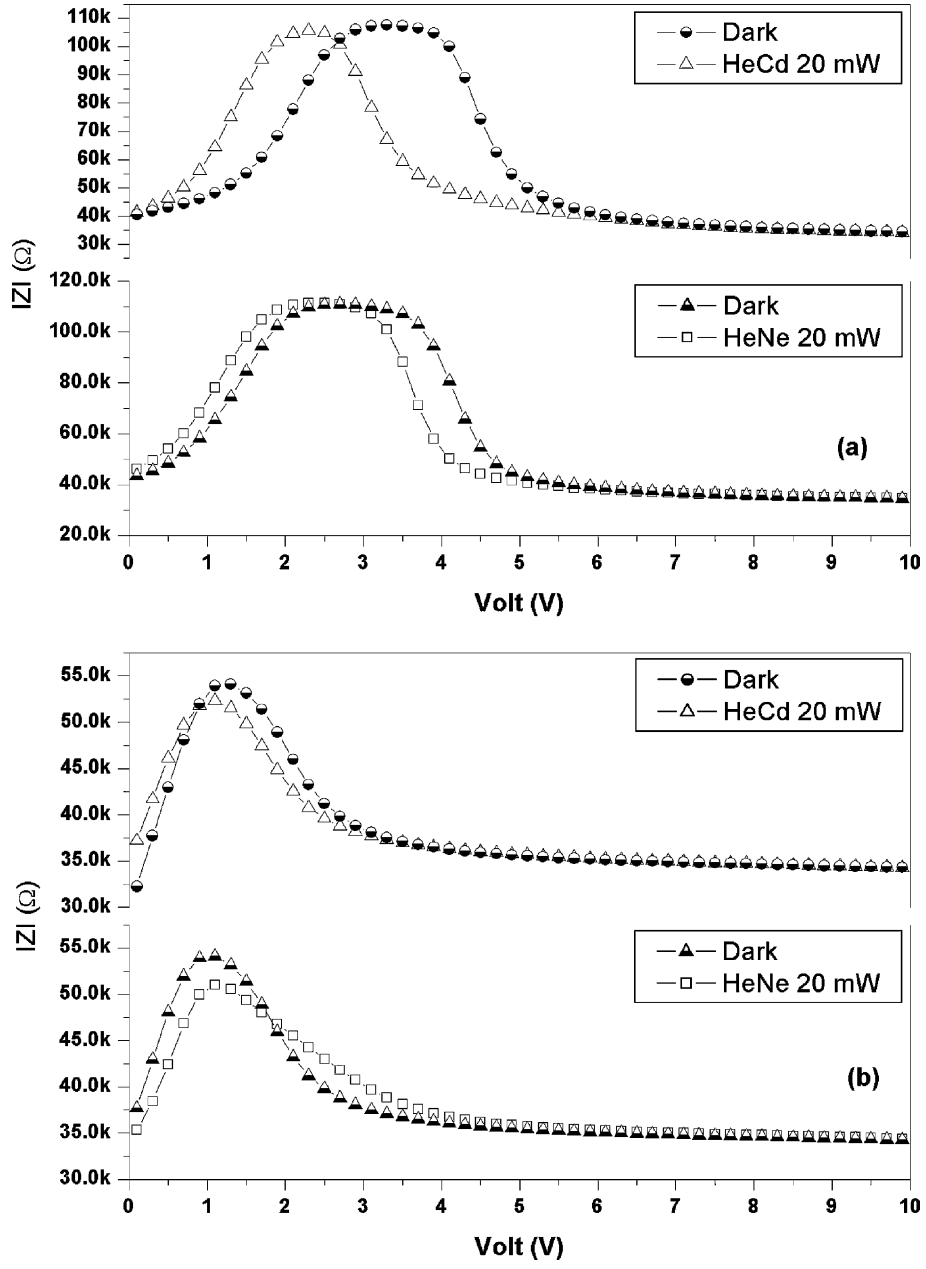

Fig. 5. Dependency of impedance on applied voltage for (a) homogenous cell; (b) homeotropic cell.

Table 1. Variation of $\Delta\varepsilon$ with respect to the spot frequencies reveals that HG orientation has p-type property at low frequencies and as the frequency increases dielectric anisotropy character shifts to n-type. Unlike HG type, HT has an n-type character at low frequencies and it shifts to p-type with frequency rise as in mirror symmetry to the other type of preliminary orientation and $\Delta\varepsilon$ values are relatively high in HG type design indeed. This is because the applied electric field is perpendicular to the overall orientation axis of molecules and field–molecule interaction takes place in an easier manner due to molecules' long axis dominance. In addition, laser illumination brings about a decrease in $\Delta\varepsilon$ values in both types of the reorientations, Table 1. Only He–Cd pumping was analyzed in this aim since its absorbance was more, however, the other laser would obviously exhibit the same behavior with less magnitude. Order parameter, S, of the sample cells are given in Table 2 at various circumstances. In order to make a quantitative comparison, it seems good to refer to the order parameter of pure E7 under non-illuminated circumstance, which is calculated to be at the order of 0.35 in our approach. Also, extinction coefficients of the dye doped samples are presented in Fig. 7 from where the corresponding value of the absorbance mode of the laser could be attained.

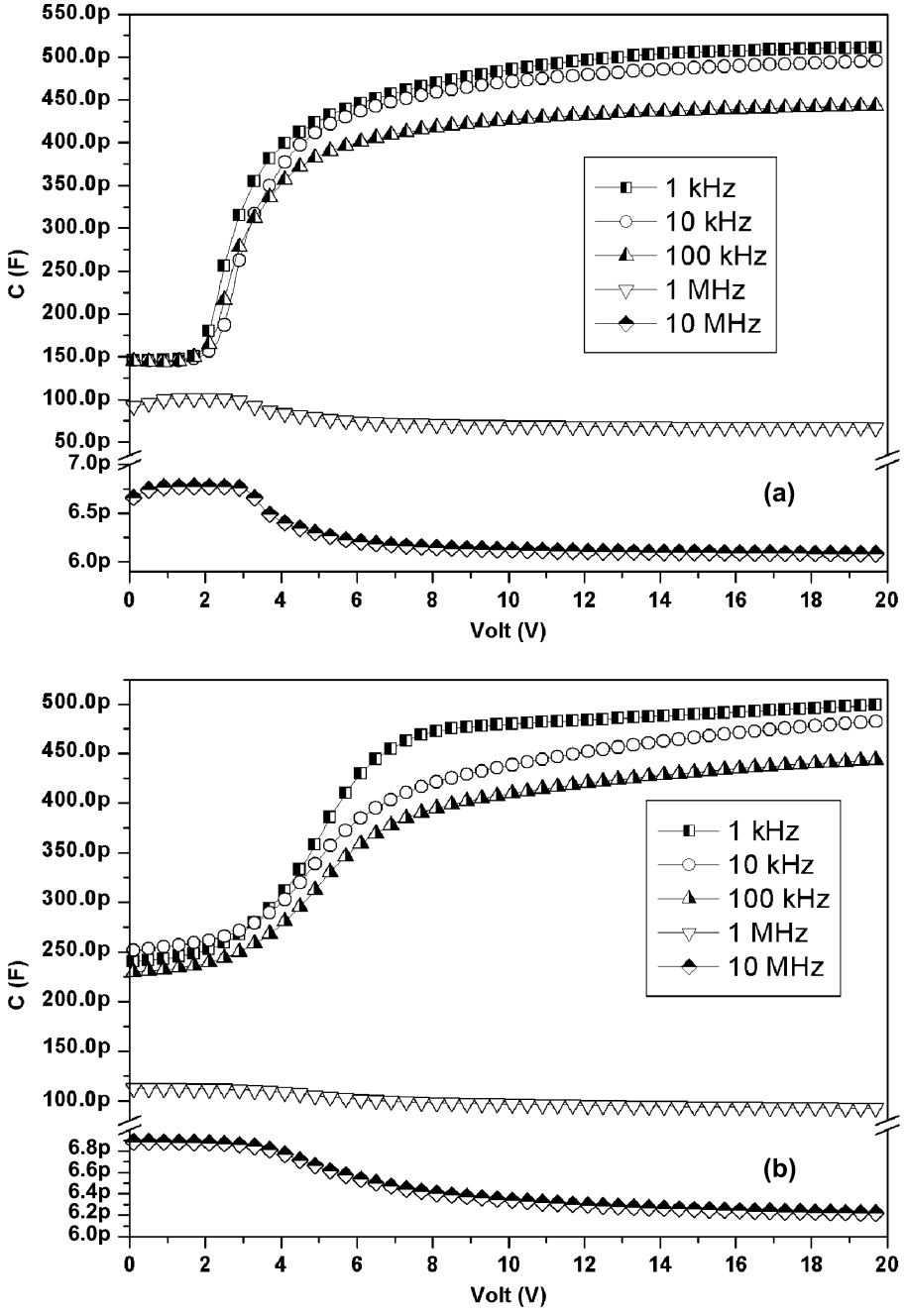

Fig. 6. Dependency of capacitance on applied voltage at various spot frequencies for (a) homogenous cell; (b) homeotropic cell.

4. Conclusion

The popular importance of mentioned experiments comes from the fact that LC are appropriate materials for recording information potentially with high resolution. They also have application areas in displays, optical switches, phase retarders, filters etc. Preparation of the LC cell is of critical importance depending on your aim and two main preliminary orientations are possible. Controversial ideas are still going on about the stages and respective strength of photo induced reorientation mechanism depending on the added agents and construction details. From our point of view, our measurements fill some portion of the ongoing discussion in such a way as to how electronic properties get modulated by molecule–laser and molecule–electric field interactions depending on the preliminary orientation of the samples.

As a brief look for the reorienting mechanisms of the used dyes MR is the azo dye component of the composite system and this dye experiences *trans–cis* photo isomerization when it is exposed to laser

Table 1
Dependency of dielectric anisotropy on the spot frequency for homogenous and homeotropic cells under dark and laser illuminated conditions

$\Delta\varepsilon$	HG		HT	
	Dark	20 mW, He–Cd	Dark	20 mW, He–Cd
1 kHz	13.36	13.19	−9.53	−7.44
10 kHz	12.82	12.21	−7.43	−7.17
100 kHz	11.09	11.07	−7.09	−6.42
1 MHz	−1.25	−1.21	0.63	0.61
10 MHz	−0.026	−0.021	0.021	0.016

Table 2
Order parameter, S, for homogenous and homeotropic cells at dark and laser illuminated conditions

S	HG		HT	
	Dark	20 mW, He–Cd	Dark	20 mW, He–Cd
1 kHz	0.805	0.803	0.740	0.682
10 kHz	0.798	0.789	0.682	0.673
100 kHz	0.771	0.770	0.670	0.644
1 MHz	0.077	0.065	0.141	0.149
10 MHz	0.520	0.516	0.484	0.488

illumination. The absorbance of light by dye molecules causes these molecules to become V shaped with 120° and spatial change of dye molecules reinforces the molecular orientation of neighbor LC molecules by frictional forces. The other component DB14 is an anthroquinone derivative dye and it contributes to reorientation via Janossy effect where the starting point is the interaction between LC molecules and the excited dye molecules. It is assumed that the mean field acting on the dye molecules is different when the dye molecules are in their ground state and when they are in their excited state. This assumption brings about a modified version of optical torque. If the dye molecules are in their excited state, this means that angular momentum of dye molecules are increased by pumping laser. That is why host molecules behave in the way of minimizing their angular momentum so that total angular momentum should be conserved and this could be realized by their reorientation. In our hybrid system, these two mechanisms hold together due to the composite usage of two dyes. One of the novelties of this work comes from this composition enabling the applicability of two different pumping wavelengths on the same sample. The other goal is the optimization possibility of potential new designs for LC based optoelectronic devices with DST, which is successfully applied as a characterization tool for understanding the molecule scale events in such systems.

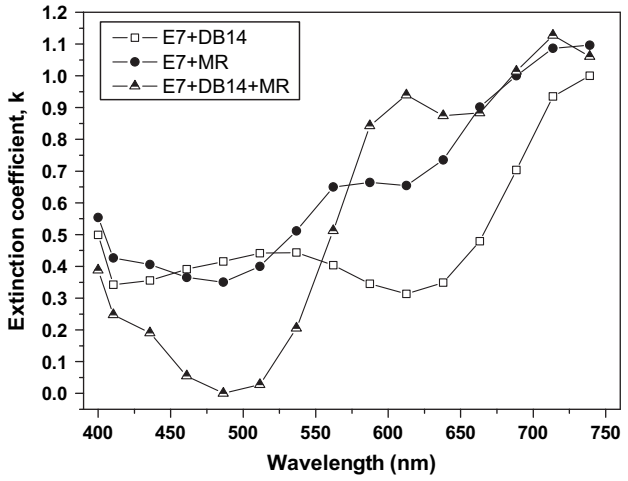

Fig. 7. Extinction coefficient versus wavelength plot for the dye doped samples in the visible range.

Acknowledgments

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