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NLO Properties of Poled Azocarbazole-Epoxy Composites

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Azocarbazole dyes are organic molecules that have already shown potential in nonlinear optical applications in host-guest systems. These molecules should be covalently bound to a host polymer network. This can be easily achieved if the host polymer is an epoxy resin. The work reports synthesis and properties of four new azocarbazoles dyes bearing a hydroxy function, which enables binding to epoxy resin.

Keywords Azocarbazoles; epoxy resin composites; nonlinear optics

Introduction

For the least three past decades the organic systems were extensively studied for their non-linear optics (NLO) properties. The most popular systems consist of a host polymer doped with physically dispersed guest dye molecules [1]. The host polymer should be optically transparent and without NLO traits. In this way, all non-linear properties arise from dispersed NLO dye molecules. NLO performance of such materials is usually attenuated by either aggregation or crystallization of dye molecules. A typical remedy to this inconvenience is substitution of an aliphatic or other bulky side group to the dye, which prevents long range organisation. The other approach depends on chemical binding of the dye molecule to the host polymer backbone. This procedure is almost effortless if the host polymer initially exists in from a liquid epoxy resin. NLO dye molecules (possessing appropriate ligands), can be chemically incorporated in the polymer network during epoxy resin setting process. Chemical binding of the dye molecule together with epoxy system leads to superior properties over the same dye but dispersed only physically [2]. There exists a variety of ligands enabling binding to epoxy resins, among the other the hydroxyl group. In this work are reported synthesis and properties of four azocarbazole dyes bearing such function. Properties of these dyes were theoretically calculated prior to the synthesis and afterwards confronted with experimental findings.

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Dye Synthesis

All chemicals were purchased from Aldrich or Fluka and used as supplied. The azocarbazole dyes were obtained in two-stage reaction. Since there was no common solvent for necessary reactants, the reaction has to be carried out in a biphasic system of immiscible liquids. In the first step hot, concentrated hydrochloric acid was added into suspension of nitroaniline derivative in water and solution containing sodium nitrite in water was slowly added. After 30 min solution was filtered to remove residues of aniline derivative. In the second step the solution, now containing diazonium salt, was poured to solution of N-hydroxyalkyl derivatives of carbazole in a mixture of n-buthanol and iso-buthanol. Both solutions were vigorously stirred to provide large contact interface between two phases containing reactants. During the coupling reaction (Fig. 1), maintained for 24 hours in 40°C. Their progress was monitored through TLC. The synthesised dye precipitated and it was filtered off. According to the method described above four compounds the following compounds were synthesised.

3-(2′-Chloro-4′-nitrophenylazo)-9-(β-hydroxyethyl)-carbazole (dye 1). yield = 80%, m.p. = 251°C

IR (KBr) ν [cm^{-1}], 3397 ($\nu_{O\text{-}H}$), 3097, 2955 ($\nu_{Ar\text{-}H}$), 1626, 1599 ($\nu_{C=C}$), 1460, 1437 ($\nu_{C\text{-}H}$), 1529, 1240 ($\nu_{N=N}$), 1041, 748 ($\nu_{C\text{-}Cl}$), 723 (γ_{CH_2})

^{1}H-NMR (300 MHz), δ, [ppm], 1,29 (d,2H), 2,47 (d,2H), 3,90 (d,2H), 4.44 (t,2H), 7,52 (dt,1H), 7,67 (dt,1H), 7,76 (dd,1H), 7,89 (d,1H), 7,92 (m,3H), 8,56 (d,1H), 8,80 (d,1H)

3-(2′,4′-Dinitrophenylazo)-9-(β-hydroxyethyl)-carbazole (dye 2). yield = 61%, m.p. = 247°C

IR (KBr) ν [cm^{-1}], 3364 ($\nu_{O\text{-}H}$), 3094, 2942 ($\nu_{Ar\text{-}H}$), 1599, 1224 ($\nu_{N=N}$), 1532, 1339 (ν_{NO_2}), 1130, 1049 ($\nu_{C\text{-}O}$), 752 (γ_{CH_2})

^{1}H-NMR (300 MHz), δ, [ppm], 1,24 (d,2H), 2,47 (d,1H), 3,89 (d,2H), 4,43 (t,2H), 7,52 (dt,1H), 7,66 (dt,1H), 7,78 (dd,1H), 7,89 (d,1H), 7,95 (m,3H), 8,55 (d,1H), 8,79 (d,1H)

3-(4′-Cyanophenylazo)-2-hydroxy-9-carbazole (dye 3). yield = 46%, m.p. = 235°C

IR (KBr) ν [cm^{-1}], 3364 ($\nu_{O\text{-}H}$), 3098, 2960 ($\nu_{Ar\text{-}H}$), 2229 (ν_{CN}), 1600, 1240 ($\nu_{N=N}$), 1463, 1418 ($\nu_{C\text{-}H}$), 747 (γ_{CH_2})

^{1}H-NMR (300 MHz), δ, [ppm], 1,28 (d,1H), 6,96 (dt,1H), 7,25 (dt,1H), 7,49 (dt,1H), 7,78 (dd,1H), 7,87 (d,1H), 8,01 (m,3H), 8,64 (d,1H)

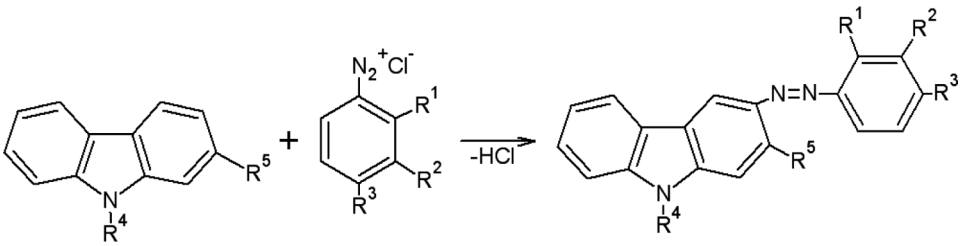

Figure 1. Scheme of the synthesis of azocarbazole dyes. *dye* (1): $R^1 = Cl$, $R^3 = NO_2$, $R^4 = C_2H_2OH$, *dye* (2) $R^1 = NO_2$, $R^3 = NO_2$, $R^4 = C_2H_2OH$, *dye* (3) $R^3 = CN$, $R^5 = OH$, *dye* (4) $R^2 = CN$, $R^3 = CN$, $R^5 = OH$.

3-(3′,4′-Dicyanophenylazo)-2-hydroxy-9-carbazole (dye 4). yield = 47%, m.p. = 245°C

IR (KBr) ν [cm^{-1}], 3304 ($\nu_{O\text{-}H}$), 3100, 2957 ($\nu_{Ar\text{-}H}$), 2228 (ν_{CN}), 1595, 1243 ($\nu_{N=N}$), 1629 ($\nu_{C=C}$), 1466, 1394 ($\nu_{C\text{-}H}$), 756 (γ_{CH_2})

^{1}H-NMR (300 MHz), δ, [ppm], 1,28 (d,1H), 6,95 (dt,1H), 7,25 (dt,1H), 7,48 (dt,1H), 7,96 (d,1H), 8,10 (m,3H), 8,63 (d,1H)

Theoretical Calculations

Theoretical calculations were supported by Hyperchem package, version 7.5. The integral geometry optimization of the molecules and its complexes was performed in frame of molecular mechanics (MM^+) force field, where the lowest energy conformations are obtained. The MM^+-force field method was chosen because is very fast, may be used for large organic molecules and gives simultaneously information about total energies and molecular geometries. Geometry optimization was accomplished through AM1 (Austin Model 1) within restricted Hartree-Fock (RHF) level. As a criterion of self-consistent convergence during the numerical procedure it was chosen that the value of energy gradient should not exceeding 0,001 kcal/mol.

Intensities of optical absorption I(ω) were determined according to formula (1):

$$I(\omega) \approx \omega \sum_{k=1}^{n} \sum_{i=x,y,z} \frac{\left|\langle \Psi_{ji}^{*} \left| i\hbar \ \vec{\nabla}_r \right| \Psi_{ki} \rangle\right|^2}{\hbar^2 \left(\omega - \omega_{jk}\right)^2 + (\Gamma/2)^2} \tag{1}$$

where Ψ_j and Ψ_k^* are wave function of j-th and k-th energy levels, $i\hbar \ \vec{\nabla}_r$ stands for transition dipole momentum of molecule, $\hbar\omega_{jk} = (E_j - E_k)$ is energy difference between the ground and the excited states and ω represents frequency of the incident electromagnetic wave.

Molecular nonlinear hyperpolarizabilities β and γ were calculated using the model with so-called multilevel excitation resumed in Eqs. (2) and (3), where: K_β and K_γ are constants, g – number of transition from ground state, E_g – transition energy, $\mu_i^{(g)}$ – transition dipole component, $M_k^{(g)}$ – excited state dipole component, $M_k^{(0)}$ – ground (reference) dipole component, H – damping

$$\beta_{kij} = K_\beta \sum_{g=1}^{N} \frac{E_g^2 \left|\mu_i^{(g)}\right| \left|\mu_j^{(g)}\right| \left(\mathrm{M}_k^{(g)} - \mathrm{M}_k^{(0)}\right)}{\left(E_g^2 - 4E^2 + H^2\right)\left(E_g^2 - E^2 + H^2\right)} \tag{2}$$

$$\gamma_{klij} = K_\gamma \sum_{g=1}^{N} \frac{\left|\mu_i^{(g)} \cdot \left|\mu_j^{(g)}\right| \left|M_k^{(g)} - M_k^{(0)}\right| \left|M_l^{(g)} - M_l^{(0)}\right|\right.}{\left(E_g^2 - 4E^2 + H^2\right)} \tag{3}$$

Experimental

Absorption spectra in UV-*vis* wavelength range were measured in solvents of different polarity – from the least polar cyclohexane to the most polar acetonitrile.

Solid state thin films, containing the studied dyes, were prepared as follows. At first, the dyes were dissolved in a low molecular mass epoxy resin Epidian 6 (from Organika Sarzyna – Poland) in proportion providing 5% per resin repeating unit. Next a stoichiometric amount of the setting agent (triethylenetetramine) was added, and the mixture was smeared over ITO covered glass substrate. After complete setting, samples were oriented by corona-poling, at 75°C, 7 keV applied for 5 minutes and for additional 2 minutes until the temperature didn't drop to the ambient.

Components $\chi^{(2)}_{333}$ and $\chi^{(2)}_{3333}$ of second and third order nonlinear susceptibilities tensors were measured using reflection electro-optic method, adapted from [3]. This approach was sufficient supposing $C_{v\infty}$ symmetry of the samples [4]. The sample was covered with vacuum evaporated aluminium layer, which played simultaneously the role of electrode and reflecting mirror. Next, the sample was subjected to superposed constant E_{DC} and modulated E_{AC} electric fields. This field modulated intensity of the reflected laser beam according to Eq. (4), where *const* express a geometrical factor depended on refractive indices, incidence angle, sample thickness and initial intensity of the laser beam. The reflected laser beam intensity was measured by a photodiode and modulated portion of the signal retrieved through lock-in technique.

$$\Delta I(\omega) = const \cdot E_{AC}(\chi^{(2)}_{333} - 2E_{DC}\chi^{(3)}_{3333}) \tag{4}$$

Results and Discussion

Data obtained in results of numerical calculations performed prior to the synthesis, i.e., absorption spectra, dipole moments, and parameters describing molecules stability are collected in Table 1. Calculations were performed for isolated molecules and factors affecting peaks broadening were neglected, so one can compare only peaks position. Keeping this fact in mind, it may be concluded that simulated absorption spectra corresponded well to experimental findings as it illustrates example shown in (Fig. 2). Calculated dipole moments were substantially smaller in case of dyes 3 and 4, i.e., where hydroxy group were directly bound to the carbazole moiety. This property corresponded to observed much lower solubility of dyes 1 and 2 in less polar solvents.

Absorption edge of the studied materials appeared (in solution and in epoxy matrix) at c.a. 560 nm, what provided correct electro-optic measurements without attenuation due to optical absorption. From the other side, such absorption makes these dyes applicable for diffraction grating inscription, using YAG laser [5]. The

Table 1. Numerical simulation results – binding energy, heat of formation, and dipole moment

Parameter/dye	dye 1	dye 2	dye 3	dye 4
Binding energy (kcal/mol)	−4545.47	−4665.29	−4338.56	−4782.35
Heat of formation (kcal/mol)	417.73	330.14	253.54	249.95
Total dipole (D)	4.20	4.89	2.57	0.59

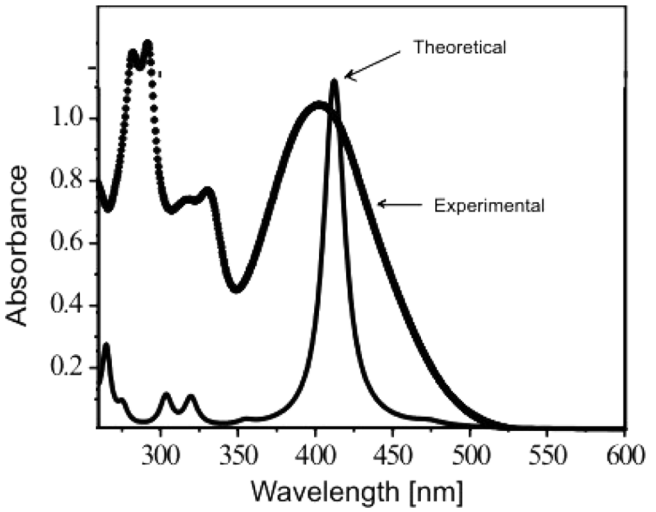

Figure 2. Comparison of theoretical and experimental spectra of dye 1.

observed solvatochromic effect was not very important, attaining not more then c.a. 60 nm of shift due to the increased solvent polarity (between cyclohexane and acetonitrile). Absorption spectra of all studied dyes are shown together in (Fig. 3).

In Table 2 are presented calculated molecular hyperpolarizabilities β and γ compared to experimentally found $\chi^{(2)}_{333}$ and $\chi^{(2)}_{3333}$. Although there does not exist a direct link between nonlinear optical properties of individual molecules and containing them bulk materials, some interesting conclusions can be drawn. Parameters $\chi^{(2)}_{3333}$ measured for macroscopic samples are more or less in same proportion with calculated γ for appropriate dyes. This is not the case for $\chi^{(2)}_{333}$ and β. Ratio between

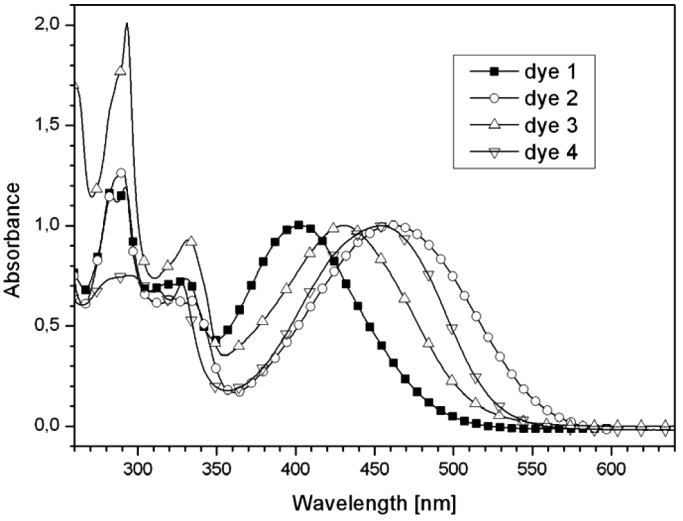

Figure 3. Absorption spectra of the studied dyes in solution in acetone. Spectra were normalized to the unity for the fundamental transition.

Table 2. Calculated molecular hyperpolarizabilities β and γ and experimentally found macroscopic parameters $\chi^{(2)}_{333}$ and $\chi^{(2)}_{3333}$

Molecule	β [a.u.] (a)	γ [$m^5 \cdot V^{-2}$] (b)	$\chi^{(2)}_{333}$ [m/V] (c)	$\chi^{(2)}_{3333}$ [$m^2 \cdot V^{-2}$] (d)	$\chi^{(2)}_{333}/\beta$ [$\times 10^{-15}$] (e)	$\chi^{(2)}_{3333}/\gamma$ [$\times 10^{14}$] (f)
dye 1	340	$7{,}16 \cdot 10^{-36}$	$2{,}9 \cdot 10^{-11}$	$2{,}8 \cdot 10^{-21}$	85	3.9
dye 2	856	$4{,}25 \cdot 10^{-36}$	$5{,}1 \cdot 10^{-11}$	$1{,}4 \cdot 10^{-21}$	60	3.3
dye 3	1961	$2{,}07 \cdot 10^{-35}$	$1{,}2 \cdot 10^{-11}$	$1{,}1 \cdot 10^{-20}$	6.1	5.3
dye 4	854	$1{,}25 \cdot 10^{-35}$	$8{,}1 \cdot 10^{-12}$	$9{,}1 \cdot 10^{-21}$	9.5	7.3

them holds separately for dyes containing hydroxyethyl (1 and 2) and hydroxy (3 and 4) side groups. In the last group values of $\chi^{(2)}_{333}$ are lower in spite of higher values of β. A possible explanation can be their lower dipole moment – a factor directly linked to corona poling efficiency. This hypothesis is hard to be accepted because of big difference between dipole moments of dye 3 and dye 4, while ratio of their $\chi^{(2)}_{333}$ and β holds. More likely dye molecules bound to epoxy matrix through hydroxyethyl group (i.e., more distanced form polymer network) can easier change their orientation during the poling process, what resulted in more important orientation on macroscopic scale.

Conclusions

There was presented efficient method of synthesis of new azocarbazole dyes of nonlinear optical properties. Obtained experimental data, although applied corona poling was not optimized, situate these dyes between typically reported so far in the literature. It was found that dyes bearing hydroxyethyl group are more efficient NLO dopants in systems based on solid state epoxy resin.

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