



Nonlinear optical activity of push–pull indolizine-based chromophores with various acceptor moieties

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ABSTRACT

For the first time the nonlinear optical (NLO) activity of indolizine-based push-pull chromophores with different acceptor moieties was studied and compared. All the chromophores demonstrate strong absorption band in the visible (orange-red) part of the spectrum, with ϵ of ca. $10^5 \text{ L}\cdot\text{cm}^{-1}\cdot\text{M}^{-1}$ notably dependent on medium polarity. Replacement of Ph-TCF acceptor by Hex-TCP one results in twofold increase of the first hyperpolarizability value. Energy gaps estimated by electrochemical methods decrease in the series $\Delta E_{1a,b} > \Delta E_{3a,b} > \Delta E_{2a,b}$ for compounds with Ph-TCF, DCM and Hex-TCP acceptors, respectively, good agreement with DFT estimations is obtained. The nonlinear optical coefficient for poled PMMA-based films, containing 20 wt% of isomeric indolizine chromophores with weaker dicyanomethylene (DCM) acceptor and with π -bridge expanded by isophorone moiety, achieves 36 pm/V, thus exceeding those for materials containing chromophores with stronger Ph-TCF or Hex-TCP acceptors and with short vinylene π -bridge.

1. Introduction

The advantages that organic nonlinear optical (NLO) materials provide as components of photonic devices stimulate research aimed at creation of new materials [1,2] in particular those based on dipolar push-pull chromophores [3,4]. Such compounds with various donor and acceptor end units separated by different π -conjugated bridges have been designed, synthesized and their NLO properties have been investigated [3–24]. Aniline [5–11,24], thiophene [10–14], pyrrole [13,14], pyrane [15], julolidine [16] moieties were widely used as donors. NLO properties of chromophores with ferrocene [17,18], tetrahydrofulvalene [19,23], carbazole [12], indolylidene [20], dihydrobenzothiazolylidene and dihydroquinolinyldiene [21,22] donor moieties were also reported. The chromophores with heterocyclic donor units have shown large values of the first hyperpolarizability – molecular quadratic NLO characteristic. However, with the exception of julolidine-based chromophores [25–27] only a few studies of

macroscopic NLO activity of push – pull systems with heterocyclic donor moiety incorporated into polymer films as guests have been described so far. Among them indolylidene- [28,29], carbazole- [30], phenoxazine- [31], phenothiazine-based chromophores [31] have been investigated for NLO activity. NLO properties of thin films of metallophthalocyanine also were studied [32,33]. Such fused π -excessive heterocyclic system as indolizine has been bypassed as donor moiety by researchers in the field of NLO materials. Indolizines have been used in the development of various functional materials [34–40], in particular, redox-active biindolizines [37,39] and macrocycles [35,36,38], components of dye-sensitized solar cells [34] and indolizines with luminescent properties [39,40] were synthesized. Recently on the basis of quantum-chemical calculations we have shown that indolizine-based chromophores with extensive π -bridges and strong acceptor moieties have high first hyperpolarizability [41]. The present work is devoted to the synthesis and the study of photophysical, thermal and electrochemical properties of chromophores with isomeric 3-methyl-2-

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phenylindolizin-1-yl (MPI-1) or 1-methyl-2-phenylindolizin-3-yl (MPI-3) donors and various acceptor moieties as well as macroscopic NLO activity of composite materials with indolizine-based chromophores as guests.

2. Experimental section

2.1. Materials and instrumentation

Organic solvents used were purified and dried according to standard methods. The melting points were determined by the differential scanning calorimetry using NETZSCH (Selb, Germany) STA449 F3 instrument. Infrared (IR) spectra were recorded on the Bruker Vector-22 FT-IR spectrometer. All NMR experiments were performed with Bruker AVANCE-600 and AVANCE-400 (600 and 400 MHz for ^1H NMR, 150 and 100 MHz for ^{13}C NMR) spectrometers. Chemical shifts (δ , in ppm) are referenced to the solvents CDCl_3 , acetone- d_6 or DMSO- d_6 . The mass spectra were obtained on Bruker UltraFlex III MALDI TOF/TOF instrument with *p*-nitroaniline as a matrix. Electronic absorption (UV–vis) spectra were registered at room temperature on a Perkin-Elmer Lambda 35 spectrometer with a scan speed 480 nm/min, using a spectral width of 1 nm. All samples were prepared as solutions in four solvents: dioxane ($E = 2.25$), chloroform ($E = 4.81$), 1,2-dichloromethane ($E = 8.93$), and acetonitrile ($E = 37.5$), with the concentrations ranging from $\sim 10^{-6}$ to $\sim 10^{-4}$ mol·L $^{-1}$, and placed in 10 mm quartz cells. Voltammograms were recorded with a BASi Epsilon potentiostat/galvanostat (USA) at 25 °C in dichloromethane solutions under dry nitrogen atmosphere. All measurements were carried out with 0.2 M Bu_4NBF_4 as the supporting electrolyte, platinum working electrode (0.02 cm 2), platinum auxiliary electrode, and Ag/AgNO $_3$ reference electrode. All potentials were referred against the ferrocenium/ferrocene redox couple. The thermal stabilities of chromophores were investigated by simultaneous thermal analysis (thermogravimetry/differential scanning calorimetry - TG/DSC) using NETZSCH (Selb, Germany) STA449 F3 instrument. Approximately 3.0–4.9 mg samples were placed in an Al crucible with a pre-hole on the lid and heated from 30 to 500 °C. The same empty crucible was used as the reference sample. High-purity argon was used with a gas flow rate of 50 mL/min. TG/DSC measurements were performed at the heating rates of 10 K/min.

2.2. Computational details

Geometry of the chromophores under study is optimized at B3LYP/6-31G* level, as B3LYP provides a recognized standard for the geometry determination. Quantum chemical calculations of first hyperpolarizability are performed by TD-DFT. DFT technique, which has proved itself as economical alternative to exact correlation methods, permits to study large size molecular systems interesting for possible applications. An extensive literature is devoted to general problems of the DFT, such as the delocalization error (see [42–45] and references therein). On the basis of the analysis of the advantages and limitations of various density functionals it has been recognized that for the reliable estimation of NLO characteristics one should use hybrid GGA functional with a percentage of the local exchange replaced by the exact HF one [46], and to overcome the problem of delocalization error it is suggested either to use range-separated (RS) density functionals [42,44,47–49] or functionals with a set of fitting parameters to determine its form on the basis of the comparison with available experimental data [50,51]. RS density functionals describe short- and long-range parts of Coulomb operator in different ways permitting the tuning of the range-separation parameter, ω [43,43,44,45], which results in the essential improvement in the prediction of first hyperpolarizability values. The popular example of the second trend - M06-2X functional, belonging to the class of high-exchange density functionals, has also proved itself well in the calculation of molecular polarizabilities [46,51]. According to accuracy

ranking established in [46] for electronic excitations and hyperpolarizabilities, representatives of both trends, CAM-B3LYP [49] and M06-2X demonstrated rather close accuracy and were recommended for establishing trends in hyperpolarizability values providing insight in chromophores properties relevant to theory-aided design [46]. Based on our previous experience [41,52], we have chosen M06-2X in this work for the calculation of electric properties – dipole moment, μ , and first hyperpolarizability, β , of chromophores with indolizine-donor moieties.

The calculation of first hyperpolarizability puts forward serious demands for the choice of the basis set. Our previous experience has demonstrated that Dunning aug-cc-pVDZ basis sets, from which polarization functions at Hydrogens are excluded provides reliable values for the first hyperpolarizability [53]; we denote this basis aug-cc-pVDZ'.

The following computational schemes are used: the geometry of the studied chromophores is optimized and the energy characteristics are calculated at the B3LYP/6–31 G(d) level; the calculations of the electric characteristics are performed at B3LYP/aug-cc-pVDZ' and M06-2X/aug-cc-pVDZ' levels, thus giving the following computational schemes: B3LYP/6–31 G(d) //M06-2X/aug-cc-pVDZ' and B3LYP/6–31 G(d) //B3LYP/aug-cc-pVDZ'.

Based on the hyperpolarizability tensor components, β_{tot} values were calculated:

$$\beta_{\text{tot}} = \sqrt{\beta_x^2 + \beta_y^2 + \beta_z^2}, \beta_i = \beta_{\text{iii}} + \frac{1}{3} \sum_{i \neq k} (\beta_{ikk} + \beta_{kik} + \beta_{kki}), i = x, y, z.$$

The calculations of molecular geometrical parameters and electric properties are performed with Jaguar program [54].

2.3. Poling and NLO measurements

Polymer films spin cast from the 7% cyclohexanone solution of the polymer composite material were poled at the corona-triode setup in the corona discharge field, voltage 6.5 kV, poling time ~ 20 min, the distance from the tungsten needle electrode to the film surface being 1 cm; the field was applied to the films heated to temperatures close to glass transition temperature, T_g . The quality of orientation was controlled by the absorption change in UV–vis spectra detected before and after poling [55]. Polymer NLO coefficients were measured by second harmonic generation (SHG) technique; pulse Nd $^{3+}$:YAG laser radiation ($\lambda = 1064$ nm, pulse duration 15 ns, power density at the sample 10 kW/cm 2 ; α -quartz (x-cut) plate served as a standard) was used. In the course of measurements it was assumed that $d_{33}/d_{13} \approx 3$.

2.4. Synthesis of chromophores

Scheme 1 shows the synthetic approach for the isomeric chromophore pairs **1a/1b**, **2a/2b**, **3a/3b**, with various acceptor moieties. 2-Dicyanomethylene-3-cyano-4,5-dimethyl-5-phenyl-2,5-dihydrofuran, Me-(TCF-Ph), was obtained by condensation of 3-hydroxy-3-phenylbutan-2-one with malononitrile in pyridine [56]. Knoevenagel condensation of isomeric aldehydes (MPI-1)CHO and (MPI-3)CHO [57–59] with Me-(TCF-Ph) acceptor in pyridine led to the chromophores **1a** and **1b**. Compounds **2a** and **2b** were synthesized in two steps: reaction of the same aldehydes with in situ obtained Me-TCP acceptor [8] and subsequent alkylation by iodohexane of the product of the first step. Alkylation of precursors of chromophores **2a** and **2b** leads to the increases of solubility of these compounds in organic solvents including cyclohexanone, which has been used for preparing of thin films of guest-host materials. This procedure is typical for the study of properties of TCP-based chromophores; the attached substituent at nitrogen of pyrrolidine ring may be also useful as a bulky group permitting to avoid aggregation [8,60]. The chromophores **3a** and **3b** were prepared according to the approach described in literature [61].

The studied chromophores appeared as highly crystalline

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