Dyes and Pigments 158 (2018) 131–141

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Composite materials containing chromophores with 3,7-(di)vinylquinoxalinone π-electron bridge doped into PMMA: Atomistic modeling and measurements of quadratic nonlinear optical activity

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ARTICLE INFO

Keywords:
NLO chromophores
Atomistic modeling
Divinylquinoxalinone bridge
Solvatochromic behavior
TD-DFT calculations
Thermostability
NLO coefficients

ABSTRACT

Two novel chromophores with dibutylaniline donor moiety, 3,7-(di)vinylquinoxalinone π-electron bridge and tricyanofuranyl or dicyanovinyl acceptor moieties are synthesized and their properties were systematically investigated. Atomistic modeling of PMMA-based composites with the developed chromophores as guests is performed and nonlinear optical activity is studied for the first time. Atomistic modeling performed in the amorphous cell has shown that chromophore content 20 wt% may be considered most favorable for achievement of optimal d_{33} values for **7-DBA-VQ$_{on}$V-TCF/PMMA** material. Various non-covalent interactions both between chromophores and polymer matrix and chromophores inter se were revealed in the course of modeling; these interactions could contribute to the relaxation stability of orientational order and thus quadratic NLO response. Composite material **7-DBA-VQ$_{on}$V-TCF/PMMA** is characterized by nonlinear-optical coefficient, d_{33}, values of 97, 111 and 47 pm/V at chromophore content of 10, 20 and 30 wt%, respectively. Thus chromophore content 20 wt% provides maximal value of NLO coefficient, what is in agreement with the obtained theoretical data. The d_{33} value for **7-DBA-VQ$_{on}$V-DCV/PMMA** is 2.5 times smaller than that for **7-DBA-VQ$_{on}$V-TCF/PMMA** at the same chromophore load (20 wt%).

1. Introduction

Organic nonlinear optical (NLO) materials engage much attention due to their attractive potential in photonic devices [1–3]. A great emphasis was paid to the rational design of chromophores with high values of first hyperpolarizability, good thermal and photochemical stabilities [4,5]. A dipolar push-pull D-π-A type structure [6–14] occupies the most important role in the creation of NLO materials. The guest-host doped materials, containing chromophores with aniline [15–18] or julolidine [19–21] donor end, 3-cyano-2-dicyanomethylene-2,5-dihydrofuran-3-yl (TCF) acceptor end and polyene [15–19] or divinylhetaryl [18,20,21] (hetaryl is thiophene or pyrrole) π-bridge exhibit significant NLO activity [22], exceeding up to 10 times [17–19] NLO activity of inorganic materials, for example, lithium niobate. NLO activity of chromophores with other π-bridges is beginning to be studied. Chromophores with fused thiophene moieties [23–25], in particular, those with π-deficient heterocyclic ring in the π-bridge [26]. are among them.

Atomistic modeling gives the opportunity to investigate polymer materials in a detailed fashion, providing structural information and feedback to the chemists and material scientists designing new chromophores. In particular, the effect of chromophore concentration on the electro-optic (EO) coefficient of polymer composites in the applied electric field was performed in a number of papers [27–34]. Atomistic Monte-Carlo simulation of the loading and orientation parameter was performed to obtain the greatest available EO activity for a given chromophore [29]. The EO coefficient of the polymer material is known to be proportional to the order parameter. In Ref. [30] molecular

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https://doi.org/10.1016/j.dyepig.2018.05.033
Received 14 February 2018; Received in revised form 15 May 2018; Accepted 15 May 2018

modeling of the effect of chromophore concentration on the EO coefficient for guest-host polymer composites was performed in the applied electric field, and good agreement with experimental data was found. The increase in the chromophore dipole moment was shown to yield a shift to lower concentrations of the peak in the EO activity [28].

Monte–Carlo simulations of the effect of the poling field on the orientation of NLO chromophores in inert polymer matrices such as poly(methyl methacrylate) (PMMA) and amorphous polycarbonate with the account of dipole–dipole electrostatic interactions of the chromophore groups were reported in Refs. [27] and [28]. The dynamics of the poling process and the effect of the poling field on the second harmonic generation (SHG) relaxation for various polymer systems was studied by fully atomistic modeling of poled guest-host NLO polymer systems at different densities [31–33]; static conformational properties, radial distribution functions, and energetics in poled and unpoled systems of PMMA doped with the NLO chromophores N,N-dimethyl-p-nitroaniline (DPNA) [31–33] and 4-(dimethyl-amino)-4-nitrostilbene (DMANS), and N,N-di-n-propyl-2,4-dinitro-1,5-diaminobenzene (DPDNDAB) were examined in Refs. [32,33].

On the basis of the molecular dynamics (MD) simulations, the PMMA polymer mobility and the static properties of the dopant DR chromophores were derived in Ref. [34]. Interactions between chromophores and the host matrix, and the structure of the host matrix were also shown to have a great influence on the local field felt by the chromophores, and therefore affect the poling efficiency. Such interactions can even play important role in the relaxation of the chromophore order after the removal of the poling field [34].

Another problem, which should be taken into account when the systems with rather high chromophore load are considered, is the chromophores linear size and related steric hindrances, experienced by the chromophores in the course of poling. In the model developed in Ref. [35] steric interactions at high chromophore densities were shown to become competitive with electrostatic ones. In Ref. [30] the reduced degree of polar order in a composite **EZ-FTC/PMMA** material was shown to be attributed to the steric hindrances due to the large size of the chromophore.

Recently on the basis of quantum chemical calculations we have shown that quinoxalinone-based chromophores with dimethyl aniline (DMA) donor and TCF acceptor are characterized by high values of first hyperpolarizability [36,37]. Such chromophores have been synthesized and they display high thermal stability and exhibit the minimal HOMO-LUMO energy gap (down to $\Delta E \approx 0.84$ eV) [38]. The present work is devoted to the study of microscopic hyperpolarizability transfer into macroscopic NLO coefficient, d_{33}, value of guest-host materials with quinoxalinone-based chromophores as guests (Fig. 1) in PMMA matrix.

2. Experimental section

2.1. Modeling details

Atomistic modeling was performed in the amorphous cell in the OPLS3 force field, which is parameterized on the basis of high-level quantum chemical calculations [39]. The modeling in the amorphous cell allows us to account for steric hindrances due to the local environment in the material. A number of molecules (oligomers and chromophores) was selected to obtain a cell size not less than the cut-off radius for non-covalent interactions; for the case under study it was 9 Å.

Here we consider composite polymer materials with polymethyl methacrylate (PMMA) matrix and two types of chromophores-guests, differing by acceptor group – **7-DBA-VQ$_{on}$V-TCF** and **7-DBA-VQ$_{on}$-DCV**. Various weight contents of **7-DBA-VQ$_{on}$V-TCF** were considered. To build the composite PMMA-based polymer the following model system was used: ten PMMA oligomers each containing sixty monomer units. The size of the oligomer provides sufficient flexibility of the chain, since the Kuhn segment length for PMMA comprises six monomer units [40].

To equilibrate the system the multistage simulation was realized with compressive NPT protocol which includes the procedure of so called simulated annealing [41]. In the course of such an annealing the system transforms from an initial state to a state with lower energy by raising the temperature and then decreasing it. The purpose of a rise in temperature during annealing is to make the system overcome energy barriers and to let the system relax to a state with a lower energy. Multistage simulation workflow details are described in Supplementary Information. Such multistage simulation allowed packing of composite polymer system in amorphous cell with density, close to real density of polymer systems. Total simulation time was 20 ns, in the course of simulation the system was heated up to 700 K and then cooled to 300 K. After relaxing the system molecular dynamics at 400 K was performed for 10 ns with 1 fs timestep.

The modeling was performed with the program packages Materials Science Suite [42] and Desmond [43].

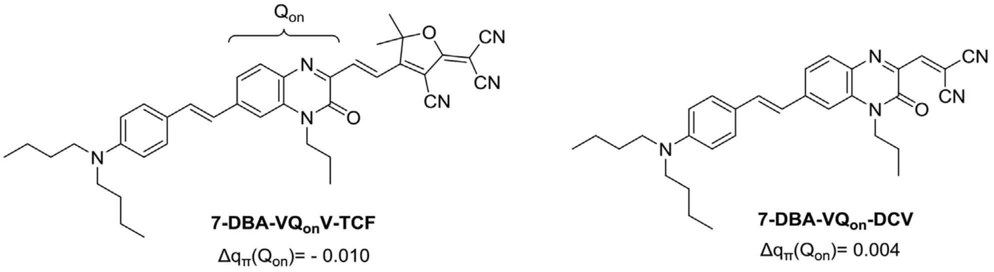
2.2. Computational methods

Chromophores structure was obtained in the course of full optimization by DFT with either B3LYP [44,45] or M06-2X [46,47] density functionals and 6-31G(d) basis sets; the calculations of the electric characteristics are performed by TD-DFT [48] with B3LYP/aug-cc-pVDZ′ and M06-2X/aug-cc-pVDZ′, thus giving the following three computational levels: M06-2X/6-31G(d)//M06-2X/aug-cc-pVDZ′, B3LYP/6-31G(d)//B3LYP/aug-cc-pVDZ′, B3LYP/6-31G(d)//M06-2X/aug-cc-pVDZ′. B3LYP density functional is known to overestimate the values of first hyperpolarazability, β [49,50]. Keeping this in mind, we have nevertheless used B3LYP for the calculations of β to perform the comparison of novel synthesized chromophores with those developed by other authors as a great amount of literature data is available which were obtained at this computational level.

The hyperpolarizability value β_{tot} is calculated as follows

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

For the data analysis we use “theoretical” convention here, assuming that the chromophore's dipole moment is expanded in Taylor series with respect to local electric field. The coordinate frame was chosen to align z-axis along the dipole moment vector of the



7-DBA-VQ$_{on}$V-TCF

$\Delta q_{\pi}(Q_{on})$= - 0.010

7-DBA-VQ$_{on}$-DCV

$\Delta q_{\pi}(Q_{on})$= 0.004

Fig. 1. Chromophores under study with total π-populations $\Delta q_{\pi}(Q_{on})$ on quinoxalinone moiety.