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Solvent effects on the photophysical properties of distyrylnaphthalene-based conjugated oligoelectrolytes

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ABSTRACT

In this study we have characterized electronic structure and photophysical properties of the new-synthetized distyrylnaphthalene DSNN derivatives in solvents of different polarity and viscosity with the use of both experimental (absorption and fluorescence spectroscopy) and theoretical (TD DFT(B3LYP)/PCM) methods. The obtained results were interpreted in terms of the reasonable scenario for the change in both geometrical conformation and charge distribution upon photoexcitation. Direct excitation of DSNN conformers with non-planar geometries concerning the conjugated backbone leads to the locally excited Franck-Condon excited states LE FC, from which the ICT state is formed. Most probably, the formation of this ICT state involves planarization and quinoidization of the conjugated core. The emissive non-relaxed LE and relaxed ICT states differ in geometry, charge distribution, polarity as well as in radiative and nonradiative decay rates. Environmental effects have a profound effect on the rate of ICT formation and also on the relative stability of these states. Thus, controlling the environment can be a very effective way of tuning the linear and nonlinear responses of the compounds studied.

1. Introduction

Molecular structure of conjugated oligoelectrolytes (COE) can be characterized as a selected number of repeat units containing an electronically delocalized backbone bearing pendant groups with ionic functionalities which improve their solubility in polar media. COE are unique because they combine the properties of organic semiconductors with the characteristic of polyelectrolytes [1]. The main advantages of COE over the conjugated polyelectrolytes are their high solubility in polar solvents (due to the presence of ionic side chains), ease of purification, well-defined structure, monodispersity, lack of batch-to batch variation and relatively high fluorescence quantum yield [2]. Among COE, oligomers based on distyrylbenzene framework (oligo(phenylenevinylene derivatives, (OPV)) have recently received particular interest from the scientific community [2–5]. This interest is basically related to the interesting and useful optoelectronic properties of OPV COE, which make them promising materials for application in a variety of emerging technologies including fabrication of optoelectronic devices (organic light-emitting diodes (OLED) technology), biosensor technology (as the light harvesting component of biosensory systems) [6,7] as well as three-dimentional imaging of biological samples [4]. The above mentioned useful optoelectronic properties of OPV-based COE result from their unique electronic structure, which can be described by D-π-A-π-D scheme, where π represents a π-conjugated bridge, whereas A and D are acceptor or donor groups, respectively. The compounds of the D-π-A-π-D structure typically undergo intramolecular charge transfer (ICT) excitation, that results in large two-photon absorption cross sections [8].

Adopting the concept of the two valence bond state model for donor-acceptor substituted conjugated systems [9,10], two mesomeric (resonance) structures: the neutral (aromatic-like) one and charge-separated (quinoid-like) form may contribute to the ground state geometry of the OPV. These forms show some differences in the geometrical structure: the quinoid form is planar and is characterized by nearly zero bond length alternation parameter (BLA), while the aromatic structure is more distorted from planarity (but nearly planar) and has higher BLA values. π-conjugated oligomers with non-degenerated electronic structures (oligothiophenes and oligophenylenevinylenes, for example) usually adopt aromatic structures in the ground state, while quinoid structures are more stable in the excited state [11].

Among the most important parameters which have to be optimized with respect to high luminescence efficiency are geometrical structure

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and electronic conjugation of the emitting species. Previous studies have postulated that the low yields of some oligophenylenevinylenes OPV are mainly the consequence of nonplanarity which enables torsional induced nonradiative deactivation [12,13].

Since fluorescence quantum yield of oligophenylenevinylenes OPV depends on their conformation, the first approach to the study of the conjugational properties of these molecules is to address the issue of the coplanarity of these systems. In the literature there is still a discrepancy concerning the planarity (conformation) of the OPV conjugated backbone [3,13–15]. Even for the unsubstituted trans-stilbene its planarity is a subject of debate [14]. The so far reported theoretical studies on electronic structure of oligoelectrolytes have not yet clarified this issue. It has been shown that generally DFT and PM3 methods yielded planar optimal geometries of the conjugated core of the model systems of OPV (donor-acceptor substituted distyrylbenzene molecules) [15], while PM6/MP2 methods predicted that the conjugated framework of the model systems was not planar (the MP2 structures have dihedral angles varying from ~25 to ~29 degrees) [3]. It seems that the differences in the geometries of conjugated backbone predicted by the DFT and MP2 methods are the result of differences in the way each quantum chemical method treats steric forces and π electron overlapping [16]. Regardless of the optimum value of the torsional angle it has been concluded that the torsional potential in stilbene analogues is shallow allowing molecules to adopt a wide range of torsional angles in solution in room temperature [14].

It has been previously proposed [8,11] for π-conjugated oligomers by several groups that direct excitation of OPV and distyrylbenzene (DSB) derivatives leads to the locally excited Franck Condon state (LE FC). The nonplanar LE FC state is relaxed quickly to the equilibrium state with a planar (or nearly planar) conformation of a more quinoid like character [13].

The luminescence efficiency of polyphenylenevinylenes (PPV) depends on competing nonradiative processes by intramolecular and intermolecular vibronic interactions. Hence, the key issue for realizing high efficient molecular optoelectronic devices is to elucidate factors affecting radiative/nonradiative relaxation behavior of these compounds [11]. Since nonradiative deactivation processes are strongly induced by intermolecular interactions, especially if the carbon backbones are able to form tight coplanar arrangements with strong intermolecular π – overlap [12], it is also very important to examine environmental effects affecting the photophysical properties of the fluorophore.

It is known that the magnitudes of two-photon absorption cross section, which reflect the probability of absorption, depend on the degree of intramolecular charge transfer (ICT) upon excitation [8]. Hence, the studies on the electronic structure which aim at characterizing electronic excitations and factors affecting them are very important from the view of their practical application of the COE. Since electronic structure of the fluorophore is manifested in its spectral characteristic, there are many previously reported studies on linear [1,3,15] and nonlinear spectroscopy [8] of oligophenylenevinylene derivatives. H. Y. Woo et al. [8] studied solvent effects on the two photon absorption of distyrylbenzene chromophores of general D-π-A-π-D structures. The maximum two photon absorption cross section has been observed in solvent of intermediate polarity (THF), while in water the two photon absorption cross section showed a substantial decrease. This decrease has been attributed by the authors to the hydrogen bonding interactions with water molecules, which can substantially modify the internal charge transfer states. Additionally, the authors concluded that specific solute-solvent interactions may also lead to the changes in the chromophore geometry and to the multichromophore aggregation.

Recent findings [4] that some distyrylbenzene- and distyrylstilbene-based COEs show high affinity to both synthetic and biological membranes open the possibility of their use in effective fluorescence imaging of living organisms. The incorporation of these compounds into membranes is accompanied by evident changes in their spectral characteristics. Moreover, the intercalation of these COE into membranes displayed ordered organization, in such a way that the long molecular of the rigid π-conjugated center axis is normal to the bilayer plane.

Due to their amphiphilic characteristics, COE exhibit tendency to aggregate in solution. The studies of J. Ortony et al. [1] indicated that self-assembly of distyrylbenzene-based COE into multichromophore aggregates, which are stabilized by hydrophobic interactions, influences their linear and nonlinear optical properties. Aggregation of this COE in aqueous solution is manifested by the increase in fluorescence lifetime, hypsochromic shift in the emission spectra, decrease in the fluorescence quantum yield as well as larger two-photon absorption upon increasing COE concentration.

The outlined above interesting optoelectronic and photophysical properties of phenylenevinylene oligoelectrolytes as well as wide possibilities of their practical application in emerging technologies motivated us to undertake experimental and theoretical studies on newly synthetized oligoelectrolytes based on distyrylnaphthalene (DSNN) framework.

In this study we have determined the electronic structure and spectral characteristic of the following DSNN derivatives: 2,6-bis(4-{N,N-bis[6-(trimethylammonium)hexyl]amino}styryl)naphthalene tetraiodide) (**DSNN-Me$_3$I**), (2,6-bis(4-{N,N-bis[6-(N-pyridine)hexyl] amino}styryl)naphthalene tetraiodide) (**DSNN-PyI**) and (2,6-bis(4-{N,N-bis[6-(N-morpholine)hexyl]amino}styryl)naphthalene (**DSNN-Morph**) in solvents of different polarity and viscosity with the use of both experimental (absorption and fluorescence spectroscopy) and theoretical (PM6, TD (DFT)/B3LYP) methods. The ionized N(Me)$_3$I and nonionized morphline groups substituted at the pendant alkiloamino groups of DSNN chromophore improved the solubility of the compounds studied allowing to probe DSNN chromophore in polar and nonpolar media.

The obtained results clearly showed that photophysical properties of the DSNN chromophore are strongly dependent on solvent polarity and viscosity, specific solute-solvent interactions as well as environmental-induced conformational changes of the conjugated backbone. These results were interpreted in terms of the reasonable scenario for the change in both geometrical conformation and charge distribution upon photoexcitation. It has been postulated that the direct excitation of the chromophores studied leads to the locally excited Franck Condon state LE FC, from which the ICT state is formed. The formation of this ICT state, most probably, involves planarization and quinoidization of the DSNN chromophore. The compounds studied may exhibit dual fluorescence from the non-relaxed LE and relaxed ICT states. These emissive non-relaxed LE and relaxed ICT states differ in geometry, charge distribution, polarity as well as in radiative and nonradiative decay rates. The relative contribution of these states to the overall fluorescence depends on environmental induced conformational and electronic changes of the conjugated backbone. The COE studied displayed lower fluorescence quantum yield in aqueous solutions, which motivated us to examine possible deexcitation routes of the compounds studied. Most probably, the torsional induced radiatonless deactivation process with the predominated C=C and C-C vibrational modes may be considered as the main excited state depopulation pathway of the compounds studied. Additionally, hydrogen bonding interactions may activate the additional depopulation channels which also affects the fluorescence quantum yield. Moreover, formation of nonfluorescent exciplex or excimers of the DSNN chromophore may also be postulated as a possible explanation for the observed lower fluorescence quantum yields in aqueous solutions.

The results obtained in this study may be relevant to the effective performance and also to rational design of the COEs with pre-defined optical and conductive properties.