

# Spectroscopic and Morphological Properties of Divinylbenzoxazolybiphenyl Thin Films

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**Abstract** The thin organic films based on 4,4'-bis-[(Z)-1-(1,3-benzoxazol-2-yl-2-ethenyl)]biphenyl and its partly fluorinated derivatives are studied. Absorption, luminescence, and excitation spectra, luminescence decay and film morphology were found to depend sensitively on the changes in molecule structure, nature and temperature of the substrate, as well as the thermovacuum deposition rate, being the origins of bad reproducibility of the optical properties of such films. Molecular aggregation with chromophore dipoles arranged parallel to each other has been observed in absorption and luminescence spectra. The fluorescence characteristics can be explained by the combination of radiation of aggregated and non-aggregated molecules. The main characteristics of the molecules under study are calculated using DFT approach. The unusual behaviour of photodegradation in fluorinated film is found.

**Keywords** Divinylbenzoxazolybiphenyl · Thin film · Luminescence · H-aggregation · Morphology

## Introduction

Complex organic compounds are now widely used in modern high-end technologies, such as field effect transistors, photovoltaic cells, electroluminescence diodes, etc. [1, 2]. Among various organic materials,  $\pi$ -conjugated molecules are the most interesting due to their peculiar optical and electronic properties. For a creation of various electronic devices, polymers and oligomers such as polyphenylenevinylenes and their manifold derivatives are widely used [3]. Using these materials thin glasslike films can be prepared by different methods in particular by printing, spin coating or thermo vacuum deposition. Molecular solids are composed of discrete molecules held together by weak van der Waals forces; as a result, the properties of the single molecule are mainly retained in the solid state. Nevertheless, in many cases optical and electrophysical properties of thin films and electronic devices made of these materials often have bad reproducibility. There is a number of origins of such a behaviour. As a rule, organic films are formed amorphous. In such films molecules are distributed rather chaotically. But, it was shown [4, 5] that the substrate temperature and the deposition rate determine molecular orientation in the film resulting in strong effect on absorption and luminescence behavior of the molecules. For example, some linear molecules can be oriented perpendicularly or parallel to the substrate surface depending on the substrate type [6] and temperature [7]. In the real devices the morphology of organic film can be changed owing to the temperature increase caused by Joule heating during the device operation.

In this paper, the effect of the changes in molecule structure, nature and temperature of the substrate, as well as the deposition rate on morphology and absorption and

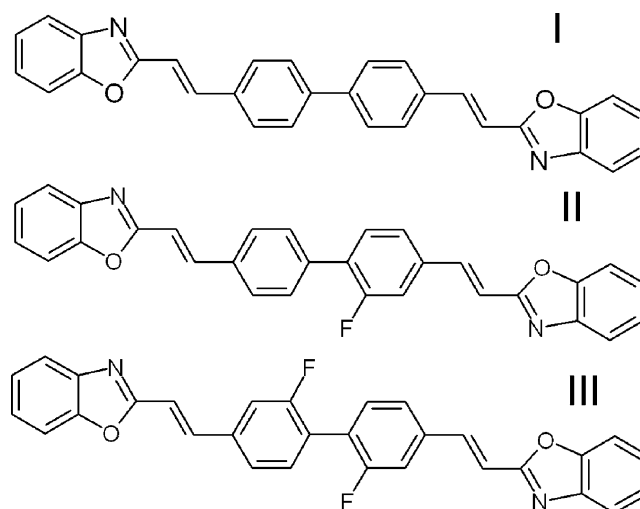
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luminescence for thin films of divinylbenzoxazolylbiphenyl and its partly fluorinated derivatives has been studied, to elucidate the origins of bad reproducibility of grown films. It was shown recently [8] that photostability of divinylbenzoxazolylbiphenyl with an aliphatic substituent is essentially lower than that of molecule without it. Also, luminescence quenching by oxygen for such molecules is different [9]. While divinylbenzoxazolylbiphenyl without an aliphatic substituent forms partly ordered films, this substance containing aliphatic substituent forms solid-state structures without any long-range order [9]. Fluorescence of fluorinated divinylbenzoxazolylbiphenyl was found [10] to be not quenched by oxygen owing to the large electronegativity of fluorine atoms. It results in the increasing of stability against oxidation. Such kind compounds are known as laser dyes as well as emitting and charge transporting materials for molecular electronic devices [11]. They can also serve as some model approach compounds of electroactive polymer like polyphenylenevinylene and its derivatives. Fluorinated electroactive molecules transforming p-type properties of materials into n-type [12] are of independent interest in molecular electronics. The high thermal stability of these molecules enables the sublimation and physical vapor deposition by thermal evaporation without any dissociation.

## Experimental

The thin films were obtained by thermo vacuum deposition on a precleaned substrate at room temperature in a vacuum evaporation unit VUP-5 (Ukraine) under vacuum of about  $10^{-4}$  Pa, typical for creation of organic electronics devices. Quartz glass, oxidized silicon and mica were used as substrates. The surface of quartz glass substrate is amorphous and inert, oxidized silicon is ordered and inert, and freshly cleaved mica has ordered structure and positive charge. The deposition rate was varied from less than 0.005 nm/sec to more than 1 nm/sec. The thickness of the films was changed from 60 to 130 nm. The quartz microbalance method is used for thickness measurements at the first deposition; then the thickness has been determined by optical absorption method (except for silicon substrate). The chemical structures of compounds under study are presented in Fig. 1. The synthesis of these compounds is described in [8, 13]. Before deposition, the material has been purified by gradient sublimation. Molecules II and III differ from molecule I by the presence of one or two fluorine atoms in diphenyl ortho positions correspondingly. Optical absorption and luminescence spectra were recorded using a spectrophotometer Cary 500 Scan UV–VIS–NIR (Varian) and a fluorometer SFL-1211A (Solar TII, Belarus), respectively. Fluorescence decay was measured by a special spectrofluorometer with



**Fig. 1** Molecular structures of substances under study. Compound I: 4,4'-bis-[(Z)-1-(1,3-benzoxazol-2-yl-2-ethenyl)] biphenyl. Compound II: 4,4'-bis-[(Z)-1-(1,3-benzoxazol-2-yl-2-ethenyl)]-2-fluorobiphenyl. Compound III: 4,4'-bis-[(Z)-1-(1,3-benzoxazol-2-yl-2-ethenyl)]-2,2'-difluorobiphenyl

a correlated photon counting. Scanning atomic force microscope pictures have been obtained with Nanoscope IIID (Veeco, USA) microscope equipped with J-scanner in a contact or tapping mode in air at room temperature. Degradation measurements have been performed using He-Cd laser (15 mW, 325 nm) and photodiode.

## Calculation details

The gas phase ground state molecular geometries were fully optimized separately in the neutral, anion and cation states, by using density functional theory (DFT) with the B3LYP hybrid functional at the basis set level of 6–31G(d) as implemented in Gaussian 03 quantum chemical package [14]. The calculations on the anionic and cationic species have been performed using unrestricted B3LYP formalism. The default thresholds and algorithms have been selected. In recent years, DFT (and its time-dependent extension TD-DFT) has emerged as a reliable standard tool for the theoretical study of geometrical and electronic properties (as IP, EA, band gap, electronic excitation spectrum) and recent works demonstrate good accuracy for a wide range of systems. This technique is applicable to fairly large molecules and metal complexes [15–18]. Frontier orbitals, IP, EA, polarizability and main electronic energies have been calculated.

## Results and discussion

Quantum chemical calculations show, that for free divinylbenzoxazolylbiphenyl molecules fluorine introduction in

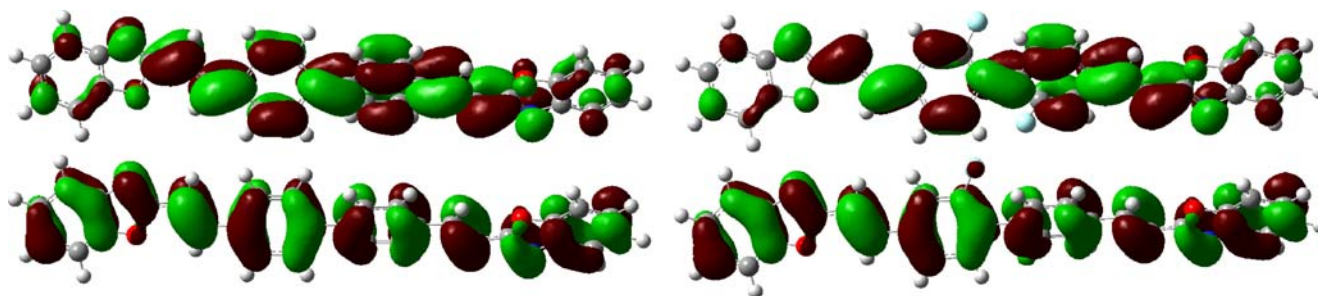
orto-positions of biphenyl leads to a considerable change of electrostatic potential of a molecule, redistributing electronic density mainly from the nearest carbon to fluorine (the partial charge on the fluorine atom in compound III equals  $-0.292$ , whereas the partial charge on the hydrogen atom in the same position in compound I equals  $+0.139$ ). The analysis of electronic structure of the highest occupied and the lowest unoccupied molecular orbitals shows that at considered fluorination they are not changed, and fluorine atoms are not involved in the  $\pi$ -conjugation (Fig. 2). On the other side, after electronic transition the highest density of electronic cloud in LUMO is observed only at diphenyl and vinyl groups (Fig. 2). Also, fluorination causes some changes in ionization potential (6.48 and 6.61 eV), electron affinity (1.37 and 1.49 eV), polarizability (0.81 and 1.66 D) and in an angle between phenyl rings of biphenyl (34.75 and 38.79 degrees) for compound I and III correspondingly. The obtained data indicates that fluorine electronegativity can change the character of interaction with neighboring molecules and, therefore, can result in the changes of spectral and morphological properties.

Absorption and luminescence spectra of substances under study at different conditions are presented in Fig. 3. The solutions exhibit intense fluorescence, originating from the electronically allowed  $1A_g \rightarrow 1B_u$  transition. Absorption spectra for nonpolar toluene solutions are nonstructured while fluorescence spectra are structured with a gradual decreasing of vibrational structure after replacing hydrogen atoms by fluorine indicating the corresponding vibration distortion. It can be caused either by the difference in vibration frequencies for corresponding C-H and C-F bonds or the change of angle between the planes of two phenyl rings in biphenyl, as a result of H to F substitution. Note that in diluted nonpolar solutions we can study molecules without any interchromophore interactions. Both absorption and fluorescence are hypsochromic shifted after replacing even one atom, in the manner similar to molecules with replaced all hydrogen atoms [19]. Spectra for solutions and thin films are different. The shift of absorption and fluorescence spectra for obtained films relative to solutions increases with fluorination indicating a stronger overall electronic interaction in fluorinated

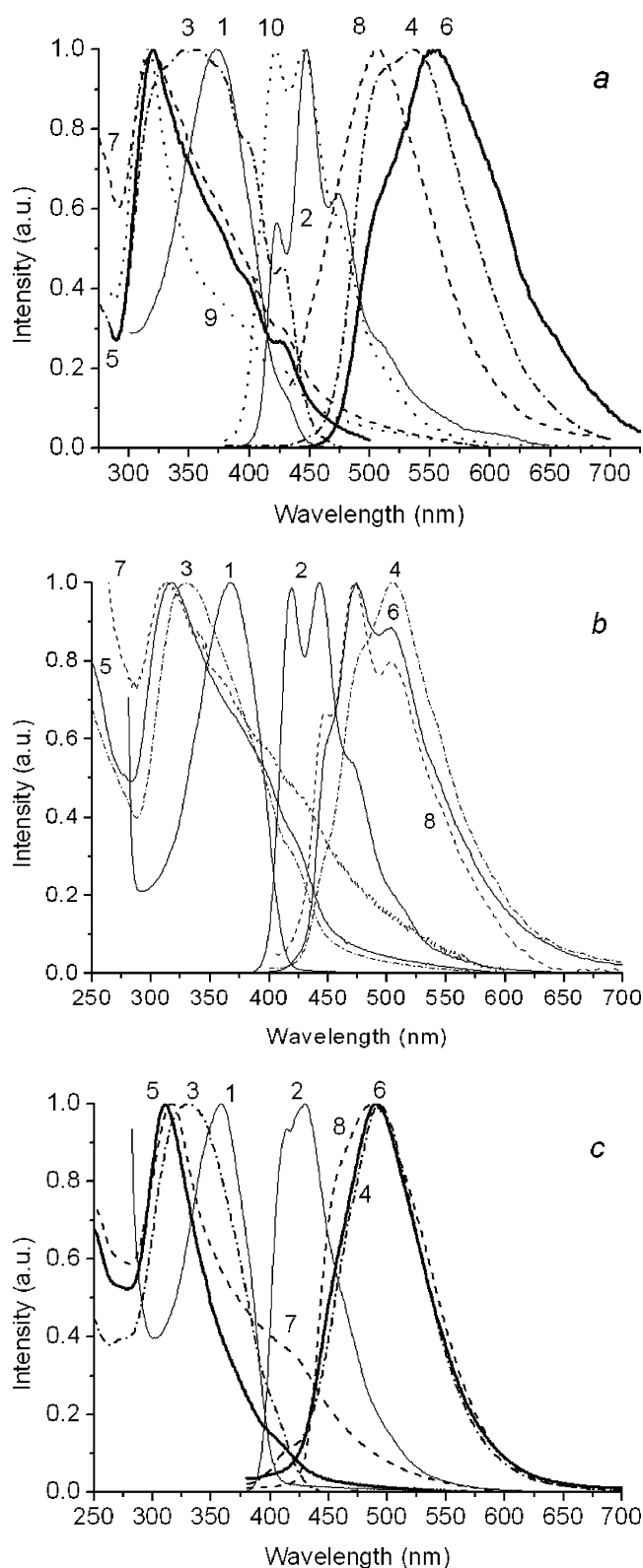
molecules. For all compounds absorption and fluorescence spectra depend sensitively on deposition rate and the temperature of the substrate. In the case of fast deposition (1 nm/sec or faster) the absorption spectra are blue shifted and fluorescence spectra are red shifted with a bell-shaped broadened form. As a rule, at fast deposition amorphous films are formed. The absorption spectra of slow (0.01 nm/sec) deposited films are situated at the same place as for fastly deposited film but left-skewed with a blue shifted maximum. The observed shape of this spectrum can be explained by at least two kinds of  $\pi$ - $\pi^*$  electronic transitions in the studied films [9, 20, 21]. One is the transition in H-aggregated chromophores ( $\lambda_{\max} \sim 320$  nm for compound I) with parallel dipole-dipole arrangement and the other is in isolated chromophores ( $\lambda_{\max} \sim 370$  nm for compound I). Most of the conjugated oligomers is known to crystallize in the so-called herringbone structure [22, 23], in which the molecular dipoles are nearly parallel. Formation of such physical aggregates results in energy lowering and splitting of the states. According to Davydov's theory [24] molecular dimers where molecules are arranged in parallel to each other, the lowest unoccupied orbital of the molecule gives rise to two exciton states, and transition from the ground state to the Davydov lowest exciton band is forbidden yielding a blue shift of the absorption spectrum. Note that molecular single crystals show a weak pure excitonic transition, intense vibronic bands, and quantum yields as high as several tens per cent [21].

The deposition of organics on hot substrate allows to grow thin films close to the thermodynamic equilibrium resulting in ordered structures on the deposited organic layer [25]. Slow deposition of substances under study on  $120^\circ\text{C}$  heated substrate also forms structures similar to deposited on room temperature substrate, but the character of ordering is somewhat different that is expressed in the increasing of longwave shoulder and a long intense tail in the absorption spectrum (see Fig. 3, curve 7).

The presence of aggregated and non-aggregated forms in thin film is confirmed by excitation spectra. As can be seen for the film I in Fig. 4, the excitation spectra differ from absorption spectra. They are not left-skewed and are closer



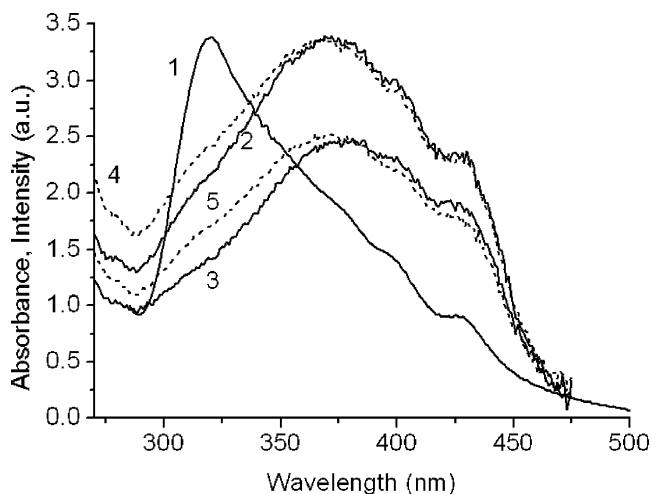
**Fig. 2** HOMO (lower) and LUMO (upper) for I (left) and III (right)



**Fig. 3** Absorption (1,3,5,7,9) and fluorescence (2,4,6,8,10) spectra for thin films of compound I **a**, II **b** and III **c**. Solution (1,2); film vacuum deposited at 1 nm/sec (3,4) and 0.01 nm/sec (5, 6) at room temperature of the substrate; film vacuum deposited at 0.01 nm/sec (7, 8) at the substrate temperature of 120°C; film vacuum deposited at 0.005 nm/sec (9) at room temperature of the substrate; polystyrene film with imbedded substance spin coated on the substrate (10)

to the absorption spectrum of a solution though with a feature in a long-wavelength shoulder. This difference indicates that fluorescence yield of H-aggregated molecules is much less than non-aggregated. The contribution of aggregated and non-aggregated luminescence can be clearly derived at short wavelengths. As a rule, H-aggregates have very low fluorescence quantum yield because its forbidden nature. H-type dimer or a non-fluorescent molecular aggregate containing more than two molecules can become slightly fluorescent due to deviations of the molecules from their positions. As a result, we observe mainly fluorescence of non-aggregated molecules. While heating the intensity of these spectra decreases in all region, owing to apparently decreasing of absorption and emission. The fluorescence decrease under heating of compound I film was found to be reversible [9].

While left-skewed absorption spectra are connected with H-aggregation, fluorescence spectra of all compounds film are strongly red shifted and broadened. The only exception is the fluorescence spectrum of thin film of the substance imbedded into polystyrene matrix (see Fig. 3a, curve 10). It fully coincides with solution spectrum (curve 2) with clearly resolved vibrational structure. It means that molecular properties are determined not only by the type of phase but also by the interaction between molecule chromophores. As a rule,  $\pi$ -conjugated molecules in pure solid-state



**Fig. 4** Absorption (1) and excitation (2–5) spectra registered at 500 (2,3) and 560 nm (4,5) at temperatures 20 (2,4) and 100°C (3,5) for compound I

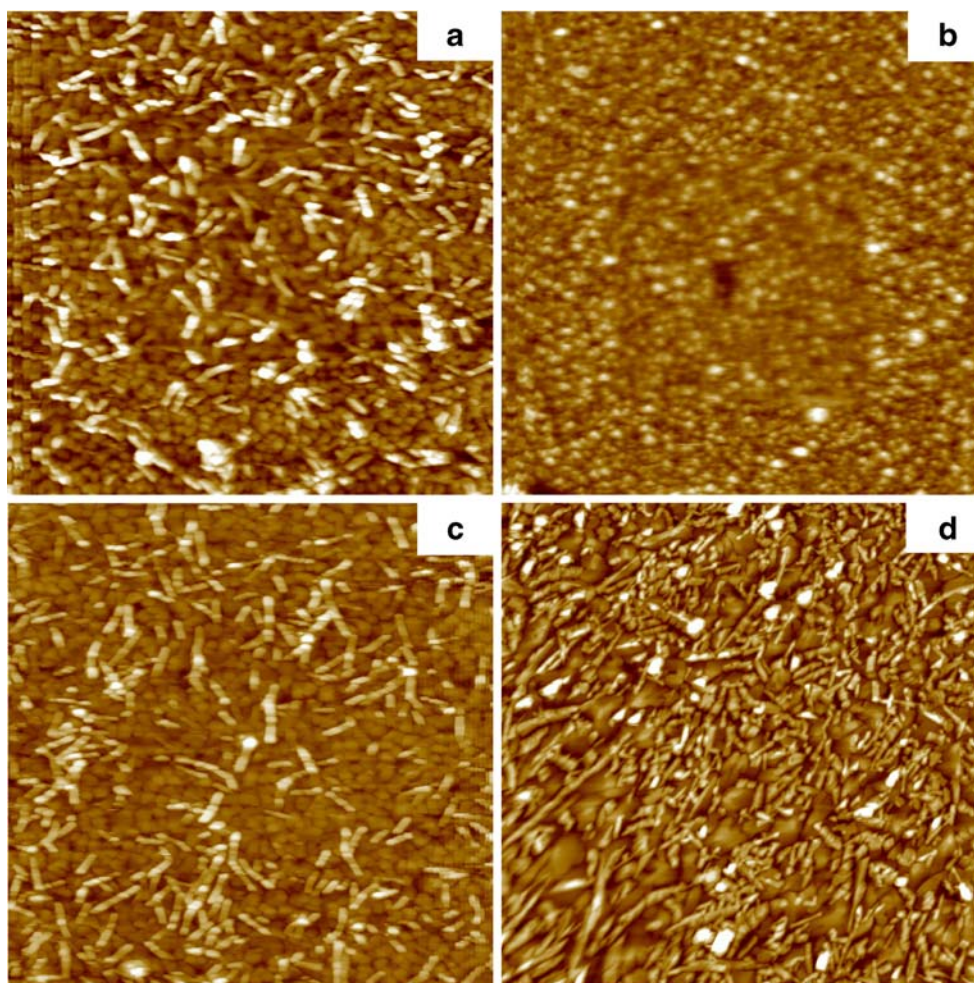
**Table 1** Fluorescence decay (nsec) of monomer (450 nm) and aggregate (550 nm) parts for thin film of compound III at different deposition conditions. The contribution value is presented in brackets

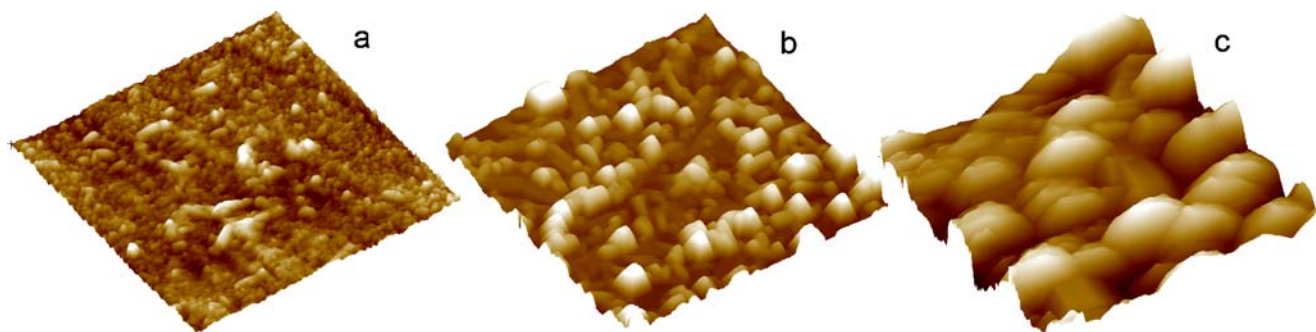
	monomer	aggregate
fast	0.7 (33.78)	1 (37.25)
	2.28 (58.01)	2.75 (55.78)
	7.51 (8.22)	10.26 (6.97)
slow	0.14 (15.13)	4.59 (36.35)
	3.51 (30.45)	13.27 (63.65)
	10.54 (54.43)	
hot slow	2.94 (17.5)	4.54 (34.15)
	7.77 (82.5)	8.63 (65.85)

structures tend to have  $\pi$ - $\pi$  interactions among the planar  $\pi$ -conjugated backbones, which lead to the formation of molecular aggregates and often result in red-shifted luminescence spectra [26, 27]. For compound I in Fig. 3 we can see a maximum at 560 nm and a feature at 500 nm which can apparently be ascribed to aggregate and monomer emission correspondingly. The observed shift of the thin

film luminescence spectrum relative to solution one is less for compound with more amount of fluorine atoms. The formation of more ordered structures caused by low rate deposition gives rise to these spectra tend to the solution curves. The presence of vibrational structure shows that fluorescence is not connected with the formation of excimer or charge transfer complex. To observe emission after exciting the aggregate, energy must migrate and eventually transfer to a monomer through exciton hopping followed by monomers either emit or decay nonradiatively. The unusual emission properties of H-aggregates have been theoretically studied in terms of a model Hamiltonian developed in [28, 29] for pinwheel aggregates. The observed differences can be explained partly by the formation of pinwheel chiral and achiral type aggregates [29]. Another explanation may include the formation of Frenkel and intermolecular charge transfer excitons [30]. In any case, all the above data make clear the main origins of bad reproducibility of optical properties in these films.

The fluorescence decay measurements of compound III films were carried out by exciting mainly monomer ( $\lambda_{\text{ex}}=410$  nm) species and recording the fluorescence emission of

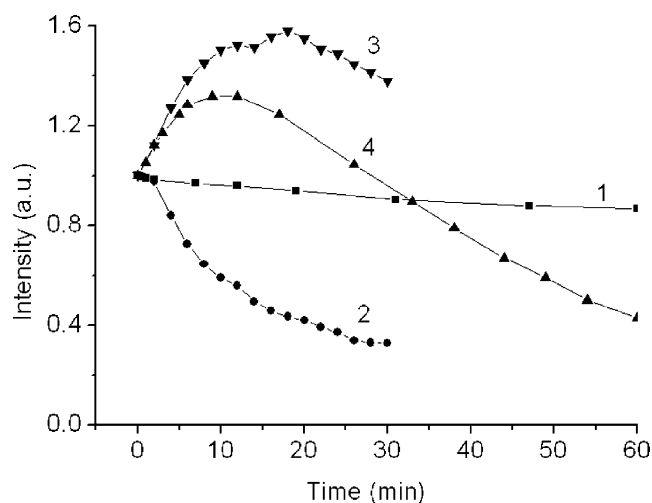
**Fig. 5** AFM topography images of a  $10 \times 10 \mu\text{m}^2$  region of the compound I film grown on quartz glass **a**, oxydized silicon **b**, and mica at room temperature **c** and  $120^\circ\text{C}$  heated mica **d** substrates; maximal z scale is 0–100 nm



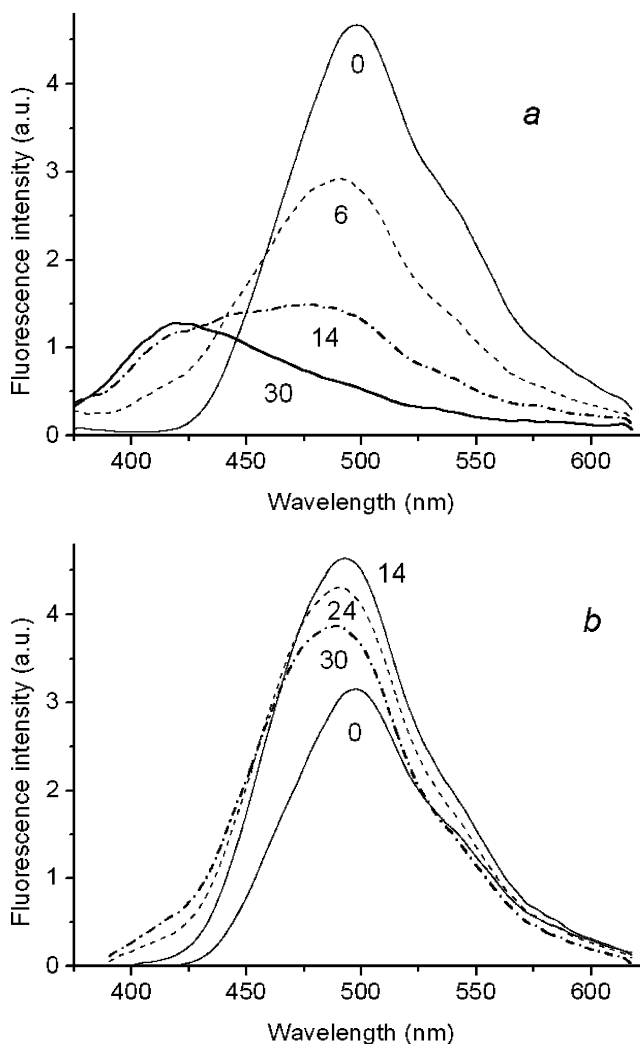
**Fig. 6** AFM topography images of a  $5 \times 5 \mu\text{m}^2$  region of compound III film deposited fast **a**, slowly at room temperature quartz substrate **b** and slowly on hot quartz substrate **c**; maximal  $z$  value is 100 nm (*left*), 300 nm (*central*), and 500 nm (*right*)

the monomer ( $\lambda_{\text{em}}=450$  nm) and aggregate ( $\lambda_{\text{em}}=550$  nm) species. It is found that both decay curves fit double- or even three-exponential functions (see Table 1). But, in solution we observe only one-exponential fluorescence decay being essentially faster (0.77 and 0.85 ns for I and III correspondingly) and independent on excitation and registration wavelengths. In the case of fast film deposition the fast decay components are prevailing for both monomer and aggregate species. Actually, in fastly deposited films we observe mainly monomer fluorescence. The fast components are close for low rate deposited films. The observed two or three components in fluorescence decay may be connected with the contribution of both aggregated and non-aggregated components, exciton hopping between two neighboring molecules, energy transfer processes, chiral and achiral aggregates. The heating of slowly deposited film from room temperature to  $100^\circ\text{C}$  was found [9] to result in the reversible decrease of both components in fluorescence decay for both monomer and aggregate emission. Such behaviour can be explained by enhancing of

intermolecular nonradiative transitions as well as by changing the proportions of aggregated and free molecules in the formation of luminescence spectrum i.e by transformation of luminescence sites.



**Fig. 7** Photoluminescence photodegradation decay of compound I (1) and III (2–4) for thin films deposited slowly (1, 2), quickly (3), and slowly on hot substrate (4). The fluorescence intensity is integral over all spectrum



**Fig. 8** Fluorescence spectra of compound III under irradiation by He-Cd laser during different time (in minutes near curves) for thin films deposited slowly (**a**) and quickly (**b**)

The observed spectral and luminescent changes are consistent with morphology studies. Commonly, the resulting dynamics of molecular aggregation is difficult to control and to predict. Morphologically diverse nanoaggregates can be obtained upon modulation of the surface electric field. Figure 5 illustrates the difference in morphology of thin films (compound I) thermo vacuum deposited at the same slow rate on quartz, oxidized silicon and mica substrates. The interaction of organic molecules with a substrate surface determines many properties of the grown thin film. If the substrate is inert such as quartz glass or oxidized silicon, the interaction of molecules with the substrate is very weak (van der Waals type; physisorption) and the properties of thin films are mostly determined by intermolecular forces rather than by the interaction with the substrate. For charged mica substrates, strong chemical interactions can be observed. As a rule, the initial ordering is gradually lost in thin films with thickness exceeding one-three monolayers [31]. Figure 5 shows that the deposition of the film with the same rate on heated mica and on oxidized silicon results in morphology strongly differed from others. On the oxidized silicon we can observe spherical aggregates, while on the heated mica polycrystalline film is clearly observed. Also we can see a strong difference in morphology depending on the deposition rate (Fig. 6). The quick deposition results in the formation of amorphous film with small averaged grains about less than 20–50 nm, the slow deposition gives partially aggregated films with averaged grains up to 200 nm. Grains on heated substrate reach 500 nm and more. The position of aggregated molecules relative to the substrate depends on its temperature. The thin films of the studied compounds conserve their morphology for a long time. Though the changes in the electrostatic distribution induces a change in the solid-state arrangement due to interactions of the local carbon-fluorine dipole moments, no visible difference in film morphology of fluorinated (compound III) and non-fluorinated (compound I) molecules was observed.

Figure 7 illustrates photodegradation of I and III films. It can be seen that photodegradation of substance I film is rather typical. It is slow and practically weakly depending on the deposition rate. The photodegradation curves of substance III films depend on the deposition rate. The initial photodegradation during 30–60 min is rather fast and then slow. Degradation of slow deposited film is typical, but degradation of other films has some growth period. But, the spectral transformations (Fig. 8) are different showing two bands. Apparently, the molecular structure is changed under light irradiation. The fluorescence of this compound in the gas phase was found [10] to be not quenched by oxygen owing to the large electronegativity of fluorine atoms. From the data presented in Fig. 7 and 8, the observed stability of this compound seems to be less than that of non

fluorinated compound. As a whole, the nature of the observed behaviour is not clear yet and needs further studies.

## Conclusions

The origins of bad reproducibility of the optical properties of grown organic films based on 4,4'-bis-[(Z)-1-(1,3-benzoxazol-2-yl-2-ethenyl)]biphenyl and its partly fluorinated derivatives are elucidated. Absorption, luminescence, and excitation spectra, luminescence decay and film morphology were found to depend strongly on the changes in molecule structure, nature and temperature of the substrate, as well as the thermovacuum deposition rate. Molecular aggregation with chromophores dipoles arranged parallel to each other has been observed in absorption and luminescence spectra. Both absorption and fluorescence are shifted after replacing even one hydrogen atom by fluorine. The value of the shift depends on the number of replaced atoms. Two and three exponential fluorescence decay is observed depending on deposition conditions. The fluorescence characteristics can be explained by the combination of radiation of aggregated and non-aggregated molecules. The difference in photostability behaviour was found for such fluorinated and non fluorinated compounds. The main characteristics of molecules under study are calculated using DFT approach. Some observed phenomena are arduous indeed to explain and deserve further theoretical and experimental investigations.

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