Y. Syetov[*]

Oles Honchar Dnipro National University, Dnipro, Ukraine
[*]e-mail: setov2003@yahoo.com

DUAL LUMINESCENCE OF 2,5-BIS(2-BENZOXAZOLYL)HYDROQUINONE IN THE SOLID STATE

Optical absorption and luminescence spectra of 2,5-bis(2-benzoxazolyl)hydroquinone were measured in solid state and diluted solution in nonpolar solvent. The compound is found to exhibit both normal and anomalously large Stokes shifted fluorescence in the solid state. The absorption band of solid 2,5-bis(2-benzoxazolyl)hydroquinone, which corresponds to the transition from the ground to the first excited state, demonstrates the vibronic structure similar to the vibronic structure of the molecule band in solution with the shift toward lower energy by about 0.1 eV. The position and shape of the luminescence band with a large Stokes shift are close to those observed in nonpolar solvent. The weak luminescence band in solid state demonstrates the relative intensity comparable with the measured in solution but larger Stokes shift and redistribution of the intensity toward lower energy. The observed dual fluorescence is caused by the close energies of localized excited states that correspond to enol and keto structures of the molecule. The large Stokes shift of the fluorescence originated from the keto structure of the molecule is caused by the much higher energy of the keto structure in the ground state.
Keywords: molecular crystals, excited state proton transfer, luminescence.

1. Introduction

2,5-bis(2-benzoxazolyl)hydroquinone (BBHQ) is a compound that exhibits photoinduced excited state intramolecular proton transfer (ESIPT). The ESIPT is studied extensively as a photochemical reaction and a process which can be employed in optoelectronics [1].

A molecule of 2,5-bis(2-benzoxazolyl)hydroquinone (BBHQ) has two hydrogen transfer centers but undergoes only single proton transfer [2]. In the ground state the enol form with two OH…N hydrogen bonds prevails, while ESIPT from the hydroxyl group to heterocyclic nitrogen atom occurs in the excited state resulting in formation of the keto structure where the NH bond becomes covalent while OH bond becomes hydrogen bonding (Fig. 1a). Distinguishing feature of the ESIPT in BBHQ is equilibrium of the enol and keto forms which are separated by a low energy barrier providing that ESIPT in BBHQ is reversible and causing dual fluorescence when the enol structure exhibits fluorescence with a normal Stokes shift and the keto form fluoresces with an anomalously large Stokes shift [2, 3].

A luminescence spectrum of BBHQ in the solid state has been firstly reported only in the region of the large Stokes shifted fluorescence [4]. The samples of BBHQ studied in the works [5, 6] contained chemical impurities obscuring fluorescence in the region 480-560 nm. In the present work we study absorption and fluorescence of BBHQ in the solid state and the spectra of diluted solution. The aim of the study is to determine energy states of the crystal responsible for the luminescence bands.

2. Experimental details

The BBHQ sample studied in this work was kindly provided by Prof. Anna Grabowska (Institute of Physical Chemistry, Polish Academy of Sciences). The solid powder was obtained by evaporation of solution in CCl_4 at room temperature. Measurements in solution were performed in CCl_4, the concentration was $3 \cdot 10^{-6}$ mol/l.

Absorption spectra were measured by the Shimadzu UV-3100 spectrophotometer

with the resolution of 1 nm. The absorption spectrum of solid-state BBHQ was measured in KBr pellet. Fluorescence spectra were recorded by Jasny spectrofluorimeter [7] with the resolution of 4 nm at room temperature, the excitation wavelength was 400 nm. Front-face illumination of the sample was used.

3. Results and discussion

The absorption spectrum of BBHQ in solution contains two clearly separated bands: one in the range 2.8-3.5 eV, which has broad components at about 2.99, 3.12, and 3.32 eV, and a band in the range 3.55-4.43 eV with prominent sharp vibronic components peaked at about 3.6, 3.87, and 4.05 eV (Fig. 1b). The solid sample also demonstrates the absorption spectrum comprising two bands, the first band has components at 2.9, 3.07, and 3.23 eV; the vibronic components of the second band at 3.61 and 3.79 eV are broad.

(a)   **(b)**
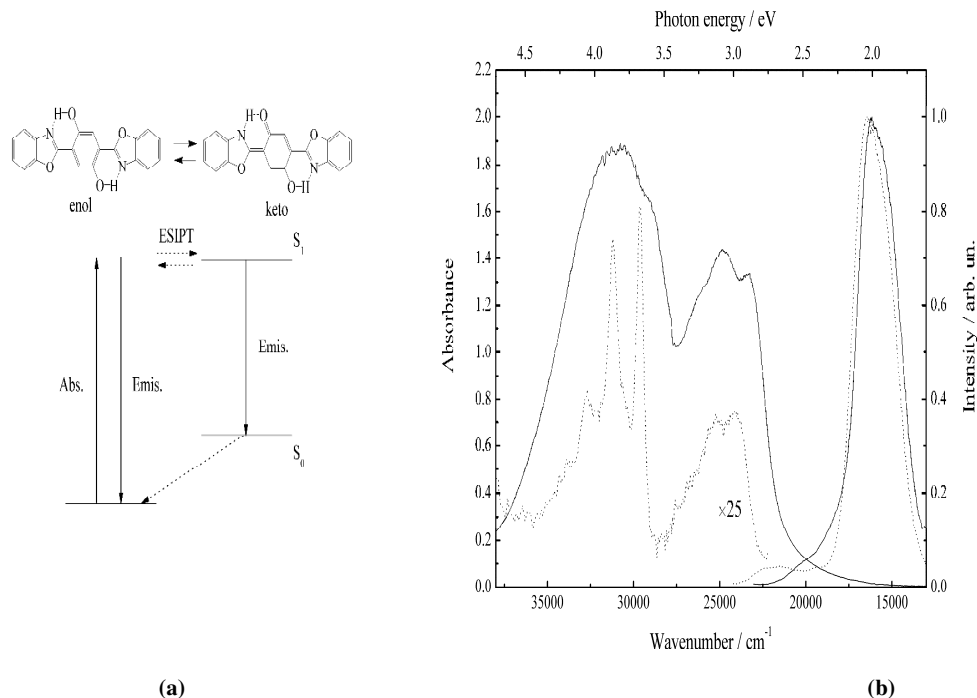
Fig. 1. (a) Structure of species of the 2,5-bis(2-benzoxazolyl)hydroquinone (BBHQ) molecule and energy diagram for the photoinduced excited-state intramolecular proton transfer in BBHQ. The solid arrows indicate absorption and emission, dashed arrows denotes proton transfer. (b) Absorption and normalized luminescence spectra of BBHQ in the solid state (solid line) and solution (dotted line).

The luminescence spectrum of BBHQ dissolved in CCl_4 at room temperature consists of an intense band with a maximum at 2.04 eV and a weak structured band from 2.36 to 2.97 eV where broad components at 2.41, 2.66, and 2.78 eV can be distinguished. The luminescence spectrum of BBHQ in the solid state contains a similar red intense band with a maximum at 2.01 eV and a broad poorly structured band which starts from 2.72 eV and overlaps with the intense band. The relative intensity of the emission in the range 2.23-2.57 eV is higher in the solid state than in the solution. The absorption and fluorescence spectra measured in CCl_4 agree with the published results for the spectra of BBHQ in nonpolar solvents and low-temperature Ar matrix. The intense emission with a

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large Stokes shift has been assigned to the keto tautomer while the band with a normal Stokes shift – to the enol structure with two OH…N hydrogen bonds [2,3]. The spectral position of the maximum of the intense luminescence band measured for the solid sample agrees well with the value reported in [4].

Quantum chemical calculations [8] show that the absorption band of solution laying in the range 2.8 – 3.5 eV is caused by transitions from the ground to first excited state and the band laying in the range 3.5 – 4.5 eV is caused by transitions from the ground to second excited state. The components of these bands are attributed to the transitions to different vibrational energy levels of the excited states. The first absorption band S_0-S_1 of polycrystalline BBHQ demonstrates the vibronic structure similar to the vibronic structure of the band of the molecule in solution. It means that electron and vibrational excitations concentrated at the same molecule and the energy spectrum is constituted by one-particle vibronic states. The frequency of the intramolecular vibration mostly involved in the transition between ground and the first excited state can be estimated from the positions of vibronic components and is found to be about 1400 cm^{-1}.

Molecular structure of BBHQ allows different orientation of the benzoxazole moieties. Rotameric structures, which possess OH…O hydrogen bonds, might exist; however, according to the quantum chemical calculations performed for an isolated molecule [8], the structure with one OH…O hydrogen bond is by ca. 0.19 eV higher in the ground state and exhibit enol-keto equilibrium similar to the species with OH…N hydrogen bonds, consequently, the number of molecules with an OH…O hydrogen bond is small in solution. The S_1 state of the rotamer has been calculated to be higher in energy than the S_1 state of the most stable structure by ca. 0.36 eV [8], implying that the rotamer is not a trap for excitons in the solid. The emission spectrum of this rotamer is expected to be shifted toward higher energy by about 0.1 eV in comparison with the spectrum of the most stable structure. According to Boltzmann distribution, the population of such states upon thermalization in the excited state is about 10^{-6}. Infrared spectrum analysis of solid state BBHQ in the region of intramolecular vibrations demonstrates that there are no considerable bands which can be assigned to the presence of such rotameric structures in the ground state [9].

Under equilibrium conditions the ratio of emission intensities can be calculated as [10]

$$I_k/I_e = (g_k f_k E^2_{S1-S0,k}/g_e f_e E^2_{S1-S0,e})\exp(-\Delta E/kT)$$

where g is a degeneracy, f is an oscillator strength, E_{S1-S0} is the transition energy, k is Boltzmann constant, T = 293 K is temperature, and ΔE is the energy difference between the enol structure and keto structure in the excited state. The degeneracy is $g_e = 1$ for the enol and $g_k = 2$ for keto structure due to the possibility of two equivalent keto structures.

To calculate integrated intensity, the observed bands were approximated by Gaussian functions attributing the components peaked below 2.2 eV (2.3 eV for the spectrum of solution) to the keto form and above 2.2 eV – to the enol form. The overall number of the Gaussians is 9, five of them are used to represent the intense band originated from the keto form, four – the weak band originated from the enol form. The ratio I_k/I_e decreases in solid from 16 to 9, and the center of gravity (mean frequency considering the spectrum as distribution function) of the weak band is shifted toward lower frequency.

Quantum chemical calculations performed for an isolated molecule [8] predict the following values for the oscillator strength and energy of transition: $f_e = 0.40$, $f_k = 0.23$,

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$E_{S1-S0,e}$ = 2.57 eV, $E_{S1-S0,k}$ = 1.97 eV, and the energy difference ΔE = -0.04 eV. The value of ΔE implies that the enol structure is more stable then the keto one in the excited state but inclusion of the vibrational energy and interaction with the solution provides satisfactory agreement with the observed intensity ratios I_k/I_e for different nonpolar and polar solvents [10]. The calculated relation $f_k E^2_{S1-S0,k}/f_k E^2_{S1-S0,e}$ varies slightly for solution in different solvents [10] and does not require the knowledge of vibrational energy so we assume that the ratio of the spontaneous emission probabilities of the electronic transitions is the same in solution and solid. Using the calculated ratio of transition probabilities for spontaneous emission $f_k E^2_{S1-S0,k}/f_k E^2_{S1-S0,e}$ and integrated intensities of the observed spectral bands, one can estimate that the keto structure is more stable than enol by about 0.06 eV in solution and 0.04 eV in the solid.

The observed large Stokes shift assessed as the difference between the positions of the maxima of the first vibronic component and fluorescence band (approximately 0.95 eV in solution and 0.89 eV in the solid) of the fluorescence originated from the keto structure of the molecule is caused by the much higher energy of the ground state S_0, but not by a large energy difference of the excited S_1 states of the enol and keto structures that agrees well with the results of the quantum chemical calculations. The calculations show that the keto structure is unstable in the ground state. There is no energy minimum corresponding to the keto structure in the ground state while the keto structure that corresponds to the energy minimum in the excited state has the energy in the ground state by 0.83 eV higher than the enol structure [8]. Efficient resonance energy transfer from the excited molecule with the keto structure to the surrounding molecules in the ground state with the enol structure is prohibited by the large difference between the energy of emission transition of the keto molecule and the energy of absorption transition of the enol molecule.

The Stokes shift of the weak fluorescence is estimated to be about 0.21 eV in solution while in the solid the corresponding difference is 0.46 eV. The increased Stokes shift of the weak fluorescence in the solid can be rationalized by involving lattice relaxation in the excited state. The lattice in the vicinity of the excited molecule undergoes a distortion due to the difference in interaction in the ground and excited state between the excited and surrounding molecules. Upon emission, the lattice remains distorted providing an additional Stokes shift. The opposite changes of the Stokes shift for the intense (decreasing shift) and weak (increasing shift) luminescence bands implies that the energy difference between the enol and keto structures decreases in the ground state in solid relatively to the difference in solution. Taking the difference between the enol and keto structures in the excited state to be 0.04 eV in the solid and 0.06 eV in solution, one can obtain that the energy difference between the enol and keto structures in the ground state decreases by about 0.2 eV in the solid.

4. Conclusions

The luminescence and absorption spectra of a substance that undergoes excited-state intramolecular proton transfer, 2,5-bis(2-benzoxazolyl)hydroquinone, were measured in the solid state. Upon photoexcitation 2,5-bis(2-benzoxazolyl)hydroquinone in the solid state exhibits emission that consists from an intense low-frequency band and a weak broad band approaching the edge of the absorption. The intense band is analogous to the luminescence band observed in nonpolar solution and originates from the keto structure formed by the excited state intramolecular proton transfer. The weak luminescence band in solid state demonstrates the relative intensity comparable with one measured in solution but larger Stokes shift and redistribution of the intensity toward lower energy.

The observed dual fluorescence is caused by the close energies of the localized excited states that correspond to the enol and keto structures of the molecule. The modification of the luminescence spectrum by intermolecular interactions offers a way for the tuning of emitting properties of organic luminescent materials.

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