Luminescence of 2,5-bis(2-benzoxazolyl)hydroquinone Molecules Adsorbed on Copper Island Film

[1]Chayka K., [1]Moiseyenko V. and [2]Mordzinski A.

[1]Dniepropetrovsk National University, 13 Naukova St., 49050 Dniepropetrovsk, Ukraine
[2]Institute of Physical Chemistry, Polish Academy of Science, 01-224 Warsaw, Poland

Abstract

Characteristics of photoluminescence spectra of polycrystalline 2,5-bis(2-benzoxazolyl)hydroquinone (BBHQ) adsorbed on a copper island film have been studied in the conditions of laser excitation. The reflectivity, transmission and luminescence spectra have been measured in the temperature range of 600 – 800 K for a number of film thicknesses and annealing conditions. It has been found that annealing of the films induces changes in the islands' morphologies. The spectral luminescence characteristics have been compared with those peculiar for the BBHQ solution in 3-metylpentan, for the BBHQ samples adsorbed on pure plane-parallel quartz plates and for the samples contained in quartz glass cell. The results have been used for interpretation of the spectra and estimation of the average amplification factor and the characteristics of molecular excitons in the crystals under investigation.

Introduction

2,5 - bis (2 - benzoxazolyl) hydroquinone (abbreviated as BBHQ) belongs to a class of substances that manifests intramolecular excited-state proton transfer. BBHQ is tautomerized in the conditions of ultraviolet excitation and shows a pronounced luminescence in green-red region, with a large Stokes shift [1]. The X-ray data show that there are two rotameric modifications of molecules in the BBHQ crystals [2]. As a substance with intramolecular proton transfer, BBHQ is very interesting from the fundamental point of view, enabling studies for dynamic mechanisms of that transfer. Moreover, BBHQ seems to be promising in connection with its possible applications in nonlinear optics, e.g., as an active element of dye lasers with ultra-short light pulses [3] or in bistable optical memory cells [4]. The fluorescence spectrum of BBHQ has been studied earlier for the both cases of nonpolar solutions [5] and solid-phase state [6, 7]. When the samples in a solid-phase state are excited in the region of 320 – 460nm, the spectrum contains a wide asymmetric band in the region of 500 – 850nm [6]. The subsequent investigation conducted under both the broadband and the laser excitations has allowed to establish dependence of the spectrum shape on the frequency and intensity of stimulating radiation [7]. However, it has failed to explain clearly the observed changes of the spectrum. The present work is thus related to studies of the luminescence spectra of BBHQ in the solid-phase state, with the application of SERS-active

substrates (here SERS means a common abbreviation for 'Surface-Enhanced Raman Scattering') based on the annealed copper island films. The purpose is to find out the nature and interpret the mentioned spectrum at the laser excitation and to estimate the characteristics of molecular excitons and the effect of "fluorescence enhancement".

Samples and experimental setup

Copper island films were fabricated with the method of vacuum vapour deposition of copper (99.95% pureness) on preliminarily cleared quartz and glass substrates (the speed 0.07 nm/s; the chamber of the vacuum post VUP-5M being at the pressure of residual gases not more than 2.5×10^{-5} Torr). The weight of the evaporated substance was 5–7 mg. In order to change characteristics of film roughness, we annealed the films [8]. This was made in vacuum (the corresponding pressure 5×10^{-5} Torr) at the temperature of 623K during 10 minutes. The BBHQ substance was deposited on the glass substrate or the annealed copper film in vacuum (the residual pressure 5×10^{-5} Torr), using the sublimation at T = 593K during 2 hours.

To control the film thickness, the roughness parameters of the copper films and the optical properties of BBHQ films, we measured their transmission, reflection and fluorescence spectra by means of modernised spectrometer DFS-12. The transmission ($T(\lambda)$) and the reflection ($R(\lambda)$) spectra were measured using a halogen lamp. The fluorescence was excited with the second optical harmonics (λ = 532 nm) of acousto-optically Q-switched YAG:Nd^{3+} laser pumped with Kr lamp (the pulse repetition rate 8 kHz; the average power 50mW). The useful signal was detected in the regime of photon counting with accumulation. The measured fluorescence spectra were not corrected for a spectral sensitivity of photomultiplier tube and a reflective power of diffraction grating. The absorption spectra $A(\lambda)$ were calculated from the transmission and

reflection ones, using the relation $R(\lambda) + A(\lambda) + T(\lambda) = 1$.

Results and interpretation

The transmission spectrum of the BBHQ film on the glass substrate obtained in the present work is shown in Fig. 1, while the fluorescence spectra measured by us earlier [7] are presented in Fig. 2.
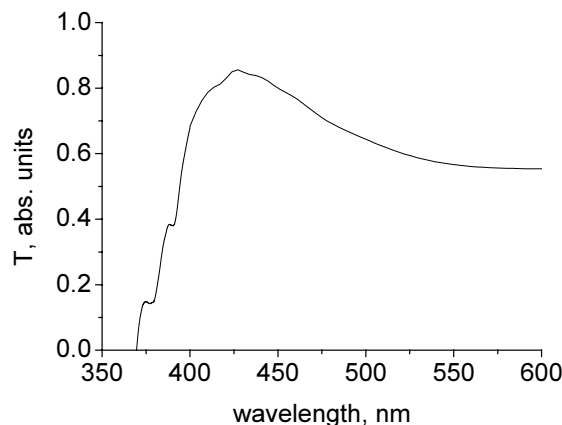
Fig. 1. Transmission spectrum of BBHQ in the solid-phase state.

The detailed comparative analysis of the fluorescence spectra shown in Fig. 2 demonstrates that the structure of the spectrum for the solid-phase state under the laser excitation is similar to that observed in the BBHQ solution in 3-metylpentan, where no proton transfer takes place (cf. curve 1 in Fig. 2 in the region of 420 – 520nm and curve 3). This means that under the laser excitation we deal with a spectrum of structural form of BBHQ without proton transfer. If the BBHQ samples in the solid-phase state are excited with the radiation of mercury lamp, the observed fluorescence spectrum is a sum of bands peculiar for the structural forms that exhibit absence (the region of 450 – 550nm) and presence (550 – 650nm) of the proton transfer [7]. The results for the fluorescence spectra of BBHQ obtained in the case of SERS-active copper substrates are shown in Fig. 3. Their shape corresponds to that detected earlier under the laser excitation [7]. However, a considerable effect of amplification is observed in this case

(see Fig. 3). The effects caused by reduction of lifetime of the excited molecules adsorbed on the metal islands have not been revealed. Quantitative analysis of the fluorescence characteristics obtained under the laser excitation allows us to determine the parameters of three spectral components (see Fig. 2, curve 3 and Fig. 3, curves 1 and 2).
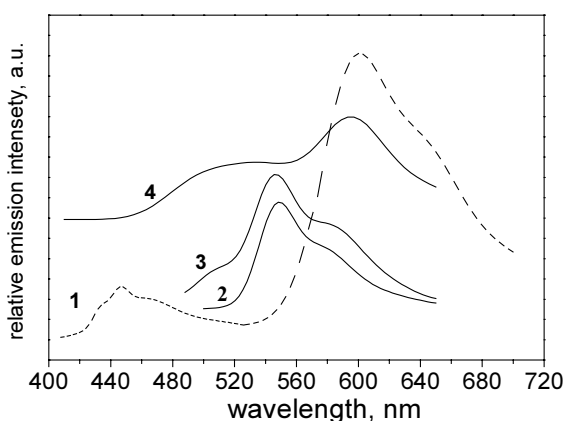
Fig. 2. Fluorescence spectra of BBHQ solution in 3-metylpentan (the molar concentration $4.8 \cdot 10^{-6}$ mol/l) (curve 1) and BBHQ in the solid phase state (curves 2, 3 and 4) [7]. The measurement conditions are as follows: curve 1 – measured with spectrofluorimeter, 2 – excited with second harmonics of YAG:Nd^{3+} laser ($\lambda = 532$nm), 3 – excited with Ar$^+$ laser ($\lambda = 488$nm) and 4 – excited with ultra-violet radiation of mercury lamp ($\lambda=350$nm and the halfwidth $\Delta\lambda_{1/2}= 50$nm).

Close positions of the centres and the halfwidths of lines that form the observed spectrum are obtained. It is established that the distances between the maxima of those spectral components are equal to $\sim 1109 \text{cm}^{-1}$ and 1305cm^{-1}. This corresponds to the frequencies of bending vibrations of BBHQ molecule in the ground electronic state [7]. The factor of "amplification" has been calculated with the formula $K = (I_2/I_1)\,(d/l)$, where I_2 and I_1 are the integrated fluorescence intensities for BBHQ deposited on the copper film and the cleaned glass surface, respectively, d is the thickness of BBHQ film, l the thickness of BBHQ layer next to a rough surface of the copper film, which

gives the amplified signal. Supposing $d \sim 500$nm, $l \sim 10$nm [9] and using the measured value $I_2/I_1 \sim 10$ (see Fig. 3), one gets a fair estimation $K = 500$ for the amplification factor. The amplification is caused by excitation of collective electronic resonances in the islands of copper film, which results in significant increase of local radiation field. Rather small value of the amplification factor should be associated with nonradiative deactivation of the excited states of molecules under the action of metal [9].
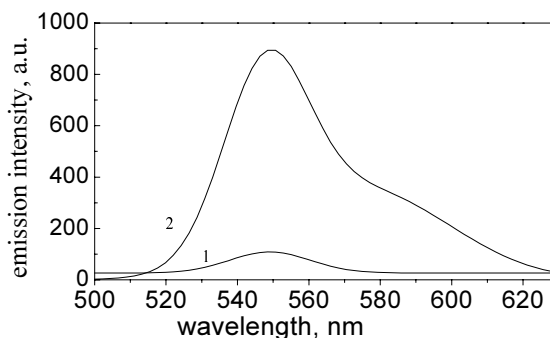
Fig. 3. Fluorescence spectra of BBHQ film deposited on the glass surface (curve 1) and the annealed copper island film (curve 2).

The observed luminescence of the BBHQ form that manifests no proton transfer is explained by transitions from the excited electron state to the vibrational levels of the ground state. The electronic excitations in molecular crystals represent Frenkel excitons. The exciton-phonon transitions are related to excitation of totally symmetric vibrations. The latter have very weak dispersion in organic crystals [10]. The observed changes in the fluorescence spectrum of BBHQ in its solid-phase state are caused by a significant downturn of energy position of the exciton energy bands for the form possessing no proton transfer. It is confirmed by the facts of rapprochement of the spectra and the values of fluorescence efficiency for the both tautomers. When the mercury lamp ($\omega > E_{ex}^{min}/\hbar$) excites the sample, the two forms contribute to the fluorescence. Then the proton transfer does not occur for the light having frequency lower than the maximum frequency of the main absorption band. As a result, the

fluorescence is completely defined by the structural form with no proton transfer. The absorption in the case of $\omega < E_{ex}^{min}/\hbar$ is caused by fluctuations of electric field in crystal. This changes the resonant frequency and the exciton-phonon interaction, which is quadratic in the displacement of molecules, and results in a long-wave absorption curve corresponding to the Urbach rule [10]. The observed absorption "tail" (see Fig. 1) is typical for the exciton absorption bands and may be explained with the dependence [10]

$$\alpha(\omega) \sim (2\pi A/|\hbar\omega - E_{ex}|)^{1/2} \exp[-(E_{ex} - \hbar\omega)/A].$$

As shown in the work [10], the exciton energy bands are completely filled at high temperatures. It can be therefore assumed that the exciton bandwidth is equal to the width of fluorescence spectrum. Within a simple model for the exciton dispersion suggested in [11], it is possible to estimate the parameters of excitons for the structural form without proton transfer, using the observed fluorescence spectra. The effective exciton mass is determined by the expression [11]

$$m = 4\hbar\Omega_{min}/(\Delta^2 + 2\Delta\,\Omega_{min})\,a^2,$$

where Ω_{max} and Ω_{min} denote respectively the frequencies of short- and long-wavelength edges of the luminescence band, $\Delta = \Omega_{max} - \Omega_{min}$ is the width of the fluorescence spectrum, and a the lattice constant ($a \sim 20$Å [12]). Knowing the effective mass, one can find the maximum group velocity $S = (\hbar\Omega_{min}/m)^{1/2}$ of excitons in crystalline lattice, the mean free path $\Lambda = S\tau_1$ and the maximum path, which the exciton passes through crystal during the lifetime $L = S\tau_2$. In the following estimations, we can take $\tau_1 = 10^{-12}$s for the average time between the collisions and assume the lifetime of the excited state of BBHQ molecule to be equal to the exciton lifetime, which is $\tau_2 = 7\times10^{-10}$s at 293 К, according to [12]. Then

the calculations yield the following exciton parameters: $m = 3.4\times10^{-31}$kg, $S = 3.8\times10^{5}$ m/s, $\Lambda = 3.8\times10^{-7}$ m and $L = 2.66\;10^{-4}$ m.

Conclusion

Thus, one can assume on the basis of the presented results that the shape of the long-wave absorption spectrum in the BBHQ polycrystals corresponds to the Urbach rule. It is revealed that the proton transfer does not occur under the laser excitation of fluorescence, if the frequency lies below the maximum frequencies of the main absorption band (i.e., in the absorption "tail" area); the fluorescence is then completely defined by the structural form that does not show proton transfer. The observed luminescence of the form characterised by the absence of proton transfer is due to transitions from the excited electron state to the vibrational levels of the ground state, which correspond to bending vibrations of the BBHQ molecule. The use of SERS-active copper substrates enables one to increase the fluorescence intensity up to 500 times. Numerical estimations of the exciton parameters for BBHQ crystals are also made.

Acknowledgement

References

1. Williams D.L. and Heller A. J. Phys. Chem. **24** (1970) 4473-4480.
2. Stenson P. Acta Chem. Scandinav. **24** (1970) 3729.
3. Chou P., McMorrow D., Aartsma T.J. and Kasha M. J. Phys. Chem. **88** (1984) 4596.
4. Munn R.W. Chemistry in Britain (1984) 518.
5. Brackmann U. et al. Chem. Phys. Lett. **110** (1984) 319.

6. Orlando C.M., Wirth J.G. and Heath D.R. Chem. Commun. **48** (1971) 1550.

7. Setov E.A., Moiseyenko V.N., Vdovin A.V., Abu Sal B. and Mordzinski A. Proc. 2nd Int. Conf. of Young Scientists 'Scientific Problems of Optics and High Technology Material Science', Kiev (2001) (Ukraine).

8. Feofanov A. et al. J. Anal. Chem. **69** (1997) 3731.

9. Surface Enhanced Raman Scattering. Ed. R.K Chang and T.E. Furtak. Moscow, Mir (1984) (in Russian).

10. Agranovich V.M. Theory of Excitons. Moscow, Nauka (1968) (in Russian).

11. Gorelik V.S. Tr. Fiz. Inst. Akad. Nauk SSSR **132** (1982) 15 (in Russian).

12. Mordzinski A., Nowak M.J. and Lipkowski J. J. Molec. Struct. **219** (1990) 209.