

**Special meeting of the Presidium
of the Russian Academy of Sciences,
the Bureau of the General Physics and Astronomy Division, RAS
and the Scientific Council of the P N Lebedev Physics Institute, RAS
on the occasion of the 110th anniversary of the birth
of Sergeĭ Ivanovich Vavilov,
and XXV Jubilee Vavilov Reading
(28 March 2001)**

A joint scientific session of the General Physics and Astronomy Division of the Russian Academy of Sciences (RAS), the Scientific Council on Luminescence of the Russian Academy of Sciences, and the United Physical Society of the Russian Federation was held in the Conference hall of the P N Lebedev Physics Institute, Russian Academy of Sciences, on 28 March 2001 at 11 a.m. The session was dedicated to the 110th anniversary of the birth of Academician Sergeĭ Ivanovich Vavilov (XXV Jubilee Vavilov Reading).

The following reports were presented at the session:

(1) **Alfimov M V** (Photochemistry Center, Russian Academy of Sciences, Moscow) “Luminescence of guest–host type organic nanostructures”;

(2) **Bolotovskĭ B M** (P N Lebedev Physics Institute, Russian Academy of Sciences, Moscow) “Vavilov–Cherenkov effect: the history of the discovery and the current status of the problem”.

An abridge version of the first report is given below.

On 28 March 2001 at 3 p.m., the scientific session (the Jubilee Vavilov Reading) was continued in a ceremonial meeting of the Presidium of the RAS, the Bureau of the General Physics and Astronomy Division of the RAS, and the Scientific Council of the P N Lebedev Physics Institute, RAS, which was held in the Conference Hall of the Presidium of the RAS.

The following reports were presented at the meeting:

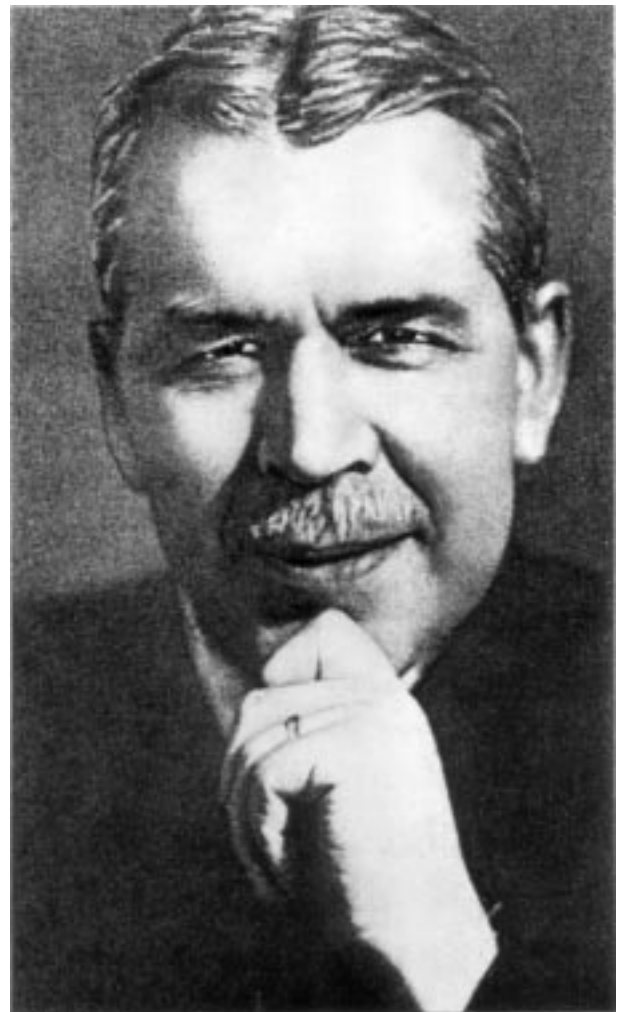
(1) **Osipov Yu S** (President of the RAS, Moscow) “Opening address”;

(2) **Ginzburg V L** (P N Lebedev Physics Institute, RAS, Moscow) “About Sergeĭ Ivanovich Vavilov”;

(3) **Krokhin O N** (P N Lebedev Physics Institute, RAS, Moscow) “S I Vavilov — the founder of the P N Lebedev Physics Institute”;

(4) **Feĭnberg E L** (P N Lebedev Physics Institute, RAS, Moscow) “Sergeĭ Ivanovich Vavilov and his time”;

(5) **Bonch-Bruevich A M** (S I Vavilov State Optical Institute, St. Petersburg) “Sergeĭ Ivanovich Vavilov in my life”.



Sergeĭ Ivanovich Vavilov
(24.03.1891 – 25.01.1951)

PACS numbers: 42.70.Jk, 78.55. –m, 81.07.Nb

DOI: 10.1070/PU2001v044n10ABEH000985

Luminescence of guest–host type organic nanostructures

M V Alfimov

Introduction

Nanotechnology as the heart of the future technological revolution increasingly often becomes the subject of basic and technological research. In this immense realm, investigations aimed at the development of biological, medical, and functional nanocomposite materials attract the particular attention of scientists. Suchlike materials may be fabricated through the inclusion of organic, metallic, semiconductor or carbon nanostructures in polymers. The interest in composite materials of this kind stems from the possibility of combining the properties of a polymer and those of a nanostructure in a material. In this case, some properties of the composite material will be close to those of a polymer, whereas others will correspond to the properties inherent in a nanostructure. By varying the dimension or the composition of a nanostructure, it is possible to change both the phase state and the constitution of the nanostructure, thereby changing many of its properties: the mobility of charge carriers, the diffusion coefficients of electron-excited states, the efficiency of luminescence, etc. For instance, the luminescence band peak of emulsion nanocrystals of silver iodide was shown to shift to the short-wavelength region by 400 cm^{-1} as the dimension of the nanocrystals decreased from 70 to 10 nm [1]. Employing nanostructures as the functional element of a nanomaterial opens up the possibility to control the properties of the nanocomposite material through the control of the nanostructure constitution. It is known [2, 3], for instance, that microdispersed particles of some of organic compounds do not fluoresce in the amorphous state, but exhibit a bright photofluorescence upon transition to the crystal state. In this case, the transformation of the amorphous particle to a crystal one may be initiated by light.

Nanostructure luminescence research is also of practical significance, because it can underlie the development of electroluminescent composite materials for light emitting diodes and materials for the sensory elements of chemical sensors.

The subject of this report is organic nanostructures (supramolecular systems) and their luminescence properties. An organic nanostructure constitutes an ensemble of molecules produced through the self-organization of molecules. Suchlike supramolecular systems are produced and retain stability due to weak intermolecular interactions: electrostatic bonds, hydrogen bonds, van der Waals and hydrophobic interactions. A single organic nanostructure can contain from several molecules to some thousands. Examples of organic nanostructures are different complexes, including ‘guest–host’ complexes, dye aggregates (H–J aggregates), etc.

Having set the task of investigating the luminescence properties of organic nanostructures and the association of these properties with the constitution and the dimension of a nanostructure, there is good reason first of all to provide the answer to the question: how does the luminescence of a nanostructure (an ensemble of molecules) differ from the luminescence of an individual molecule? Examples of distinc-

tions between the luminescence of an organic nanostructure and that of an individual molecule, which is the building block of the organic nanostructure, are numerous enough. However, the most significant distinction between the absorption and luminescence spectra of a dye in a monomeric form, on the one hand, and the corresponding spectra of the dye aggregates on the other is observed for polymethine dyes. The absorption and luminescence spectra of the aggregate are located either in the longer-wavelength (J aggregate) or in the shorter-wavelength (H aggregate) parts of the spectrum in comparison with the monomer, depending on the aggregate geometry [4, 5]. The fluorescence band widths of the J aggregates of polymethine dyes are significantly smaller than for the corresponding monomers and governed by a purely electron (0–0) transition, whereas the fluorescence bands of individual molecules comprise vibrational components as well: 0–1, 0–2, 0–3. The composition and the structure of a luminescent center made up of monoactinic molecules affect its luminescence [6, 7], and it is possible to produce nanocomposite materials with controllable spectral properties by varying the composition and the structure of the aggregate.

In this report, the results of investigation of the luminescence characteristics of the ‘guest–host’ complexes and the aggregates of these complexes are outlined. The complexes consist of ‘guest’ and ‘host’ molecules, with the ‘guest’ entering inside the ‘host’ in the formation of the complex. The strength of such complexes rises as the internal dimension of the ‘host’ approaches the external dimension of the ‘guest’.

The results of investigating two types of ‘host’ molecules are presented here — cyclodextrins and the molecules of photoreversible dyes containing crown-ether groups as a substituent.

Cyclodextrins (α , β , γ) are natural compounds whose shape resembles a basket in the game of basketball with an internal diameter of about 1 nm. For instance, beta-cyclodextrin consists of seven alpha-D-glucosidepyranose chains connected by glucoside bonds. The internal cavity of cyclodextrins is hydrophobic and is capable of sorbing organic molecules. Calculations [8] show that aromatic molecules (naphthalene, phenanthrene, fluorene, etc.) can form stable complexes with beta-cyclodextrin.

Styryl and butadiene dyes containing crown-ether substituents were first synthesized in the Photochemistry Center of the Russian Academy of Sciences. The crown-ether fragments are a flexible annular structure made up of several (4–7) twin ethylene fragments connected in a ring by heteroatoms (of oxygen, nitrogen, or sulfur). Crown-ethers form ‘guest–host’ complexes with the cations of different metals due to ionic interactions.

Complexes of cyclodextrins with aromatic molecules

The photoluminescence (fluorescence) of aromatic molecules in room-temperature solutions arises from molecular transitions from an excited singlet state to the ground state. In liquid solutions, as a rule, the phosphorescence of aromatic molecules is not observed, because oxygen molecules contained in the solution efficiently deactivate the triplet states of the aromatic molecules. On freezing the solutions (77 K) to eliminate diffusion processes, both the fluorescence and the phosphorescence of the aromatic molecules are examined experimentally. However, the same result (a simultaneous observation of fluorescence and phosphorescence) can be achieved at room temperature. Adding beta-cyclodextrin to

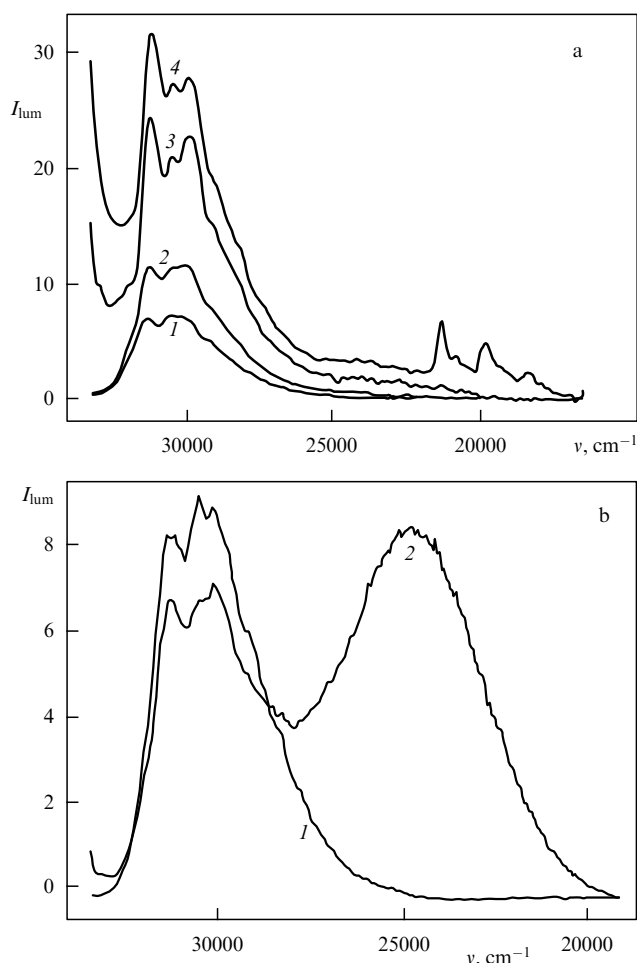


Figure 1. Transformation of octadeuterionaphthalene luminescence spectra in the medium self-organization. (a) 1 — luminescence spectrum of the naphthalene- d_8 aqueous solution ($C = 1.3 \times 10^{-3}$ M) at 294 K; 2 — with an admixture of cyclodextrin ($C = 5 \times 10^{-3}$ M); 3 — with an admixture of cyclohexane ($C = 0.01$ M); 4 — with an admixture of sodium sulfite ($C = 0.04$ M) for the chemical binding of oxygen. (b) Fluorescence spectrum of the naphthalene- d_8 saturated aqueous solution at 296 K (1) and the corresponding spectrum after the formation of a complex with β -cyclodextrin ($C = 5 \times 10^{-3}$ M) (2).

the aqueous solution of, for instance, octadeuterionaphthalene (Fig. 1a) results, as noted above, in the formation of 'guest-host' complexes. In this case, a rise in the quantum yield of fluorescence of the aromatic molecule occurs. Increasing the concentration of complexes in the solution or adding special molecules (cyclohexane, acetone, hexane, etc.) to the solution, which favor the aggregation of complexes, results in the formation of aggregates of the complexes [9]. These aggregates can range widely in dimensions (10–1000 nm), depending on the conditions. It was shown that the role of special additives which favor the aggregation of complexes consists in the formation of ternary cyclodextrin–octadeuterionaphthalene–cyclohexane complexes, whose water solubility is much lower than for cyclodextrin–octadeuterionaphthalene complexes, and therefore they efficiently aggregate to form nanostructures. In this case, the luminescence of the solution changes significantly — the quantum yield of fluorescence rises, and there appears a long-lived room-temperature phosphorescence (Fig. 1a).

Because the luminescent center in the system is octadeuterionaphthalene, the observed changes in the luminescence

of the solution are associated with self-organization in the system on addition of cyclodextrin and cyclohexane to the solution. Of special interest is a comparison between the phosphorescence spectra of the frozen solutions (77 K) of aromatic molecules and the phosphorescence spectra of aromatic molecules of the cyclodextrin–aromatic molecule–cyclohexane aggregates. The halfwidth (110 cm^{-1}) of vibrational components in the phosphorescence spectra of the aggregates of complexes turned out to be far less than the halfwidths (210 cm^{-1}) of similar lines in the phosphorescence spectra of aromatic molecules of frozen solutions [10]. Since the widths of these vibrational components remain invariable over a broad temperature range (275 K–77 K), it is safe to assume that the widths of spectral components are determined by inhomogeneous broadening. Hence it follows that the aromatic molecules included in nanostructure-organized cyclodextrin reside in a substantially more homogeneous environment than the aromatic molecules in frozen solutions. It is notable that by varying the chemical constitution of the additive in the ternary complex the possibility is raised to affect the width of the electronic–vibrational line in the phosphorescence spectrum of nanostructures made up of cyclodextrin–aromatic molecule–precipitator complexes.

The above-outlined effects of medium self-organization and changes of system's fluorescence and phosphorescence were observed in the conditions when the concentration of aromatic molecules in the solution was two orders of magnitude lower than the number density of cyclodextrin.

However, when the concentrations of aromatic molecules (octadeuterionaphthalene) and cyclodextrin in the solution are high and comparable in magnitude (10^{-1} M), a new short-lived fluorescence band appears (Fig. 1b), which peaks at 26000 cm^{-1} . This fluorescence arises from the aggregation of two cyclodextrin–octadeuterionaphthalene complexes in a unified system, so that two octadeuterionaphthalene molecules find themselves located one above the other. Suchlike dimeric complexes of aromatic molecules have been known to exhibit excimer fluorescence.

Complexes of photoreversible dyes and metal cations

An investigation was made of the luminescence of styryl and butadiene dyes containing crown-ether groups and their complexes with metal cations as substituents [11].

When dye solutions are excited by photons, the dyes exhibit fluorescence. Introducing metal salts into the solution results in the formation of complexes of the crown-fragments of the dyes with the metal cations. In this case, the dye fluorescence spectrum shifts to the short-wavelength side and the fluorescence decay time shortens several-fold (Fig. 2). The magnitude of the spectral shift is higher when the cation dimension matches that of the crown-ether cavity. By varying the cation dimension, it is possible to obtain cation–dye complexes of composition 1:1 as well as 1:2 and 2:2.

In the complexation of the *cis*-form of a dye containing two complexing groups at different ends of the molecule, the dye molecule forms an annular structure in which one metal cation forms a complex with two complexing groups of one molecule. In this case, the rotation angles of single bonds are substantially changed and the intramolecular conjugation system is broken, and the intensity of the long-wavelength electron transition lowers by a factor of 10–100 (the solution bleaches completely).

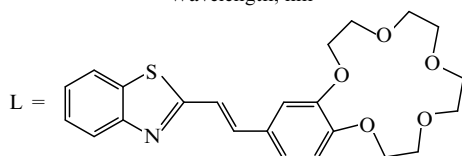
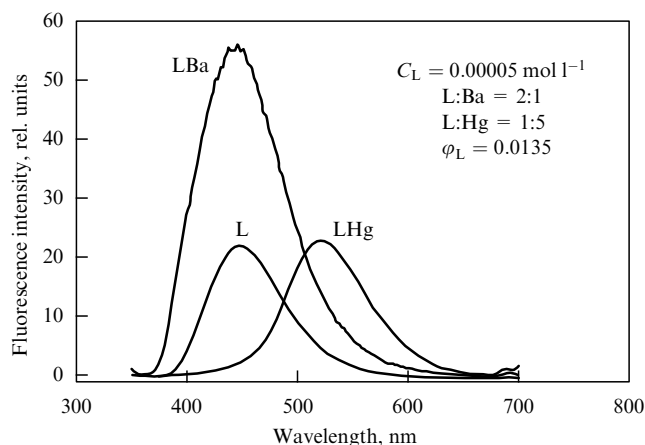


Figure 2. Fluorescence spectra of crown-containing styryl dye and its complexes with barium and mercury cations.

In the majority of dye solutions investigated, on addition of a metal salt to the solution a hypsochromic shift of absorption and fluorescence spectra occurs. In some cases, however, adding a metal salt to the solution results in the hypsochromic shift of the absorption spectrum, whereas the fluorescence spectra of the initial form of the dye and the complex coincide completely. The observed effect is attributed to the fact that the metal cation in these complexes moves, in the lifetime of excited electronic state, away from the heteroatom of the crown-ether fragment included in the conjugation chain (a recoordination occurs), and the dye fluorescence proceeds from the molecule structurally similar to the dye prior to the complex formation [12].

The dyes containing two similar complexing groups (crown-ether) or different complexing groups (crown-ether and a sulfoxyl, carboxyl group) form dye–cation complexes of composition 2:2 on addition of metal cations to the solution [13]. In this case, by varying the molecular structure and the cation dimension it is possible to finely control the complex stereostructure and change the mutual arrangement of the functional dye groups. For crown-containing styryl dyes, it has been possible to obtain stereostructures with both parallel and perpendicular arrangements of the double bonds of ethylene groups. In the complexes with a parallel arrangement of ethylene groups, during photolysis a photochemical reaction of cycloattachment proceeds with the formation of a cyclobutane ring out of two ethylene groups.

References

1. Efimov S P et al. *Dokl. Akad. Nauk SSSR* **320** 123 (1991)
2. Alfimov M V, Razumov V F *Dokl. Akad. Nauk SSSR* **260** 1383 (1981)
3. Alfimov M V et al. *Dokl. Akad. Nauk SSSR* **276** 360 (1984)
4. Bershtein K Ya, Bagatur'yants A A, Alfimov M V *Izv. Ross. Akad. Nauk Ser. Khim.* (9) 1705 (1995)
5. Bershtein K Ya, Bagatur'yants A A, Alfimov M V *Izv. Ross. Akad. Nauk Ser. Khim.* (1) 67 (1997)
6. Makhov D V, Egorov V V, Bagatur'yants A A, Alfimov M V *Chem. Phys. Lett.* **246** 371 (1995)

7. Makhov D V, Egorov V V, Bagatur'yants A A, Alfimov M V *J. Chem. Phys.* **110** 3196 (1999)
8. Nazarov V B, Avakyan V G, Vershinnikova T G, Alfimov M V *Izv. Ross. Akad. Nauk Ser. Khim.* (10) 1716 (2000) [*Russ. Chem. Bull.* **49** 1699 (2000)]
9. Nazarov V B, Gerko V I, Alfimov M V *Izv. Ross. Akad. Nauk Ser. Khim.* (9) 2225 (1996) [*Bull. Russ. Acad. Sci., Div. Chem. Sci.* **45** 2109 (1996)]
10. Nazarov V B, Gerko V I, Alfimov M V *Pis'ma Zh. Eksp. Teor. Fiz.* **65** 507 (1997) [*JETP Lett.* **65** 528 (1997)]
11. Alfimov M V, Gromov S P "Fluorescence properties of crown-containing molecules", in *Applied Fluorescence in Chemistry, Biology, and Medicine* (Eds W Rettig et al.) (Berlin: Springer-Verlag, 1999) p. 161
12. Druzhinin S I et al. *Proc. Indian Acad. Sci.* **107** 721 (1995)
13. Berzykin A V et al. *J. Am. Chem. Soc.* **114** 6381 (1992)

PACS number: **01.60. + q**

DOI: 10.1070/PU2001v044n10ABEH001039

Opening address

Yu S Osipov

Today we commemorate a remarkable date: the 110th anniversary of the birth of Academician Sergei Ivanovich Vavilov — one of the outstanding physicists of the 20th century, a talented organizer of the science in our country, a public figure and a statesman, President of the USSR Academy of Sciences during the first post-war years.

S I Vavilov was born in Moscow on 24 March 1891. After graduating from the Moscow Commercial School in 1909, he entered the Physico-Mathematical Department of Moscow University. During his university years, Vavilov attended the seminars of and worked in the laboratory led by Professor P N Lebedev — the founder of the first major Russian school of physics. It was then that Sergei Ivanovich took the general avenue of his investigations, and adopted the style and traditions of Lebedev's school. His attention was attracted by the fundamental questions of the nature of light and the light–matter interaction. That was the time when the first advances of quantum mechanics opened up the way for gaining a deeper insight into the nature of optical phenomena. S I Vavilov retained a prevailing interest in physical optics throughout his life in science.

After a brilliant graduation from Moscow University in 1914, he declined an invitation to stay at the university, which had been abandoned by the best professors. One month prior to the beginning of the First World War, Sergei Ivanovich was called up for the army.

After his return from the front in 1918, S I Vavilov worked in the Physics and Biophysics Institute supervised by Academician P P Lazarev and lectured at Moscow University and other institutes of higher education in Moscow. He began with investigations into photochemistry and progressed to photoluminescence studies and physical optics in general.

In studying the photoluminescence of solutions of complex organic dye molecules, Vavilov and his students elucidated the principal laws of absorption and emission of light by complex molecules. In particular, the dependence of fluorescence yield on the wavelength of exciting light was determined, which has come to be known as the Vavilov law. In a series of investigations into the fluorescence polarization effect, he and his co-workers discovered the dependence of the