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Life Devoted to Science

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Oleksandr Ishchenko: And Gladly Would He Learn, and Gladly Teach

Abstract
The Ukrainian school of organic dye chemistry has long received worldwide recognition. Among the scientists whose achievements embody this success is Academician Oleksandr Oleksandrovych Ishchenko. Over more than half a century of fruitful research at the Department of Color and Structure of Organic Compounds of the Institute of Organic Chemistry of the National Academy of Sciences of Ukraine, he laid the foundations for the rational design of functional dyes for light-energy conversion, particularly for various laser technologies; became one of the pioneers of polymethine ion-pair photonics; developed methodological approaches to the study of electronic absorption and fluorescence spectra using the method of moments, which provided new insights into the electronic structure of organic chromophores; and made a significant contribution to the systematic study and interpretation of the solvatochromism of polymethines of different types. The driving force behind all these achievements was his enduring passion for science – a deep desire to learn and share knowledge with future generations of researchers.
Keywords: polymethine dyes; color theory; electronic structure; material science; history of chemistry

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Олександр Іщенко: Натхненно пізнавав – натхненно навчав

Анотація
Українська школа органічних барвників давно здобула світове визнання. Серед учених, чиї досягнення уособлюють цей успіх, – академік НАН України Олександр Олександрович Іщенко. За понад півстоліття плідної наукової праці у відділі кольору та будови органічних сполук Інституту органічної хімії НАН України він заклав основи цілеспрямованого дизайну функціональних барвників для перетворювачів світлової енергії, насамперед для різноманітних лазерних технологій; став одним із піонерів фотоніки іонних пар поліметинів; розробив методологічні підходи до дослідження електронних спектрів поглинання та флуоресценції із застосуванням методу моментів, що дозволило отримати нову інформацію про електронну будову органічних хромофорів; зробив вагомий внесок у раціональне дослідження та інтерпретацію сольватохромії поліметинів різної природи. Ключовим рушієм цього успіху було його незмінне натхнення наукою, прагнення пізнавати нове й передавати знання майбутнім поколінням науковців.
Ключові слова: поліметинові барвники; теорія кольору; електронна будова; матеріалознавство; історія хімії

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■ Early Life and Education

Oleksandr Oleksandrovych Ishchenko was born on August 26, 1950, in Piskivka, Kyiv Oblast, Ukraine. Soon afterward, the family of the future scientist moved to Kyiv, which from then on became his lifelong home.

His father, Oleksandr Trokhymovych, had just retired from military service and was working as an engineer while pursuing higher education through evening studies. His mother, Larysa Hryhorivna, was a philologist and university lecturer.

In the courtyards of his Kyiv childhood, one of Oleksandr Ishchenko's first lifelong passions began to take shape – he became an ardent supporter of the Kyiv football club Dynamo. Later, during his student years (1968–1973) at the Faculty of Chemistry of Taras Shevchenko Kyiv State University, he developed other, more active and creative interests – travel and photography, and later, filming his family – his wife Valentyna, also a chemist, and son Yevgen – with a home movie camera. Together with friends, Oleksandr set out on hiking trips to the Carpathians, journeys across the lakes of Karelia, and rafting expeditions along the Chusovaya River in the Urals. Yet all these pursuits filled only the time left free from the main passion of his life – science.

Oleksandr Ishchenko was among the best students of his year. From the very beginning of his studies, he displayed a strong enthusiasm for scientific and creative work. It was this passion that led him to approach Mykhailo Kornilov and ask him to become his research supervisor. At that time, Prof. Kornilov was deeply engaged with a rapidly developing method of physicochemical analysis – NMR spectroscopy. He entrusted the young Ishchenko and his classmate and friend, Oleksandr Turov, with studying the relevant literature, particularly on the principles of the NMR spectrometer operation and the use of lanthanide shift reagents to resolve overlapping signals in ^{1}H NMR spectra – a technique of great importance in the era before high-field superconducting spectrometers became widely available. The open lecture on NMR spectroscopy prepared by the two Oleksandrs attracted undergraduate and graduate students, as well as faculty members who had completed their education before the advent of NMR spectroscopy and wished to acquaint themselves with the capabilities of this rapidly developing field. The lecture was received with great interest, and the two were even invited to present it at other venues in Kyiv.

Prof. Oleksandr Oleksandrovych Ishchenko

■ Journey into Science

After graduating from the University with distinction, Oleksandr Ishchenko – on the advice of Prof. Mykhailo Kornilov, who recognized that his student's "greatest" opinion talent lay in the field of theoretical chemistry – chose Heorhii Dyadyusha as his scientific advisor. The latter was an outstanding theoretician and one of the pioneers of quantum chemistry in Ukraine; at that time, he worked in the Department of Color and Structure of Organic Compounds at the Institute of Organic Chemistry of NAS of Ukraine.

The problems, assigned by Dr. Dyadyusha to his graduate students – Oleksandr Ishchenko, Oleksii Rykov, and Oleksii Kachkovsky – required them to acquire new knowledge in physical and quantum chemistry, as well as in computer programming. The young researchers found a creative solution: they prepared scientific presentations on the topics they needed and discussed them vigorously together.

The topic of Oleksandr Ishchenko's first dissertation research was the mathematical analysis of band shapes in the absorption and fluorescence spectra of organic dyes. By that time, the scientific community already understood that the shape of a band in an electronic spectrum provides much more information about the electronic structure of the corresponding chromophore than do the traditional parameters of the band maximum and intensity. However, no methodology yet existed that would allow a meaningful comparison of the shapes of absorption and fluorescence bands of different

dyes and the formulation of reliable conclusions based on such analysis.

The only parameter then commonly used to describe band shapes was the full width at half maximum (FWHM), which, as Oleksandr Ishchenko demonstrated in his PhD (Candidate of Sciences) thesis *"The chemical structure and absorption band width of cyanine dyes"* (1980), is not sufficiently reliable for comparing bands of markedly different shapes, especially strongly structured ones. Instead, he proposed applying mathematical analysis of spectral bands using the method of moments, defining the criteria necessary for the use of this approach, such as the required signal depth at the band edges, the separation of higher electronic transitions (in absorption spectra), and recommendations for the approximation of band edges of different shapes [1, 2].

It should be noted that the young researcher was fortunate to have convenient model systems at hand, since for cyanines (cationic polymethines) the long-wavelength electronic transition is typically well separated from the higher ones, while the shape of these long-wavelength bands can vary significantly depending on the structure of the terminal heterocyclic fragments and the difference in their electron-donating abilities. Yet this "good fortune" was multiplied by enormous effort: an extensive analysis of the literature and selection of the optimal way to represent spectral bands (a question that, even today, lacks a universal consensus for fluorescence spectra [3]); a careful choice of compounds from among thousands of dyes available in the Department of Color and Structure; hundreds of measured and digitized spectra; writing and debugging a dedicated program in the era of punch cards; exhausting "night shifts" at the Glushkov Computational Center to obtain calculation results more quickly – making corrections to the tasks and resubmitting them for processing while the queue was shorter; and, finally, the analysis of the data obtained.

The result of this tremendous work was not merely a dissertation, but a genuinely advanced tool for the analysis of molecular spectra, as well as a significant broadening of his scientific outlook and deep familiarity with the literature in his chosen field – the electronic structure, spectral properties, and applications of polymethine dyes.

At that time, one of the most active and promising areas of application for functional dyes was laser optics. The young scientist continued to learn intensively, deepening his knowledge in this field and establishing broad scientific contacts with laser physicists in Lithuania, Belarus, Russia, and Kazakhstan. He soon realized that the requirements for dyes in this area extended far beyond the classical structure-color relationships. Accordingly, it became clear that new regularities had to be uncovered – in particular, those linking the molecular structure with the lifetime of its excited state. Here, in addition to the analysis of spectral bands by the method of moments, his background in theoretical and quantum chemistry proved invaluable. A striking example of the synergy between these approaches was Oleksandr Ishchenko's classical interpretation of the differences in band shapes and excited-state lifetimes of isomeric pyrilocyanines and related compounds [4], which opened the way to the rational design of dyes with record-short lifetimes for laser applications [5, 6].

Thanks to the initiative and efforts of the young scientist, the Department of the Color and Structure of Organic Compounds acquired the best spectrofluorometer available at the time (in 1984), which enabled the launch of active studies of the fluorescence properties of polymethines – a direction he himself led. Among the first notable results of this work was the discovery that the fluorescence bands of strongly asymmetric cyanines (with respect to the electron-donating strengths of their terminal groups), unlike their absorption bands, resemble in their shape, Brooker's deviations, and vinylene shifts the fluorescence bands of the corresponding symmetric parent dyes [7], which opened the way to the design of cyanines with record-high Stokes shifts. Moreover, the fluorescence solvatochromism of both asymmetric and symmetric cyanines was found to be determined almost entirely by the solvents polarizability (n_D) and to be independent of their general (ε_D) and specific (nucleophilicity, electrophilicity) polarities [7, 8]. Oleksandr Ishchenko concluded that this result implies both an increase in the electronic symmetry of polymethines in the fluorescent S_1 state compared with the ground S_0 state and a decrease in charge alternation within the chromophore. This interpretation was corroborated by quantum-chemical calculations. It is worth noting that the fluorescent properties of polymethines, and more broadly, fluorescence spectroscopy as a powerful tool for studying organic compounds, became the subject of a brilliant plenary lecture delivered by Oleksandr Ishchenko at the All-Ukrainian Conference in Uzhhorod in 1986, dedicated to

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the 90th anniversary of the birth of Academician Andrii Ivanovych Kiprianov.

In Oleksandr Ishchenko's studies on the solvatochromism of polymethines, his broad scientific outlook and excellent theoretical background – as well as his deep understanding of solvation at the molecular level – were clearly manifested. These qualities formed the basis for his interpretation of the atypical spectral behavior of cyanines in weakly polar solvents [9]. In fact, he was one of the founders of a distinct line of research – the photonics of polymethine ion pairs and their associates.

Here, the knowledge he had gained during his student research projects proved particularly useful. Using NMR spectroscopy, he was able to experimentally determine the localization of counterions in cyanine ion pairs [10, 11] and, by analyzing aromatic solvent-induced shifts (ASIS), to show that in the first solvation shell of polymethines, the molecules of aromatic solvents are oriented predominantly parallel to the plane of the polymethine chromophore [8]. This effect proved to be so pronounced that in strongly nucleophilic pyridine, the long-wavelength absorption bands of cyanines, which undergo strong nucleophilic solvation and hence hypsochromic shifts and broadening, for example in DMF, appear similar to those observed in less polar solvents. These results served as the basis for both practical recommendations on solvent selection for the laser applications of polymethines and for subsequent studies on dye behavior in polymer matrices (composites), as well as for the use of dye-doped functional materials in light-energy conversion and quantum-electronic applications. In this latter field, Oleksandr Oleksandrovych became an internationally recognized expert; he was repeatedly invited to deliver plenary lectures at international conferences, to give lecture courses at Ben-Gurion University (Israel) and Karaganda State University (Kazakhstan), and to contribute review articles on the subject [5, 12].

The defense of his doctoral thesis in 1991, titled "*The Structure and Spectral-Luminescent Properties of Polymethine Dyes*", which later formed the basis of a monograph of the same name [13], just officially confirmed Oleksandr Ishchenko's scientific maturity and outstanding achievements in his chosen field of research. Another early marker of his success as a scientist was the awarding of the A.I. Kiprianov Prize of the NAS of Ukraine in 1997.

This essay cannot accommodate a full account of Oleksandr Ishchenko's numerous subsequent studies, reflected in more than 400 publications in scientific journals, dozens of patents, several book chapters, and four monographs. I will therefore mention only a few more of the most remarkable directions of his work.

The first of these is the study of photoconductive polymer composites, carried out in collaboration

O. O. Ishchenko (left) and M. O. Davydenko (right) showcase their laser defectoscopy device at the exhibition

with Dr.Sci. Mykola Oleksandrovych Davydenko. Among the topics of this extensive research were the influence of external electric fields on the spectral properties and electronic structure of symmetric and asymmetric polymethines in polymer matrices; the effect of the structure of dye dopants on the photoconductivity and photovoltaic characteristics of dyed polymer composites; and the development of highly efficient holographic recording media that require no protection from scattered light, among others [14, 15].

The second one, conducted in collaboration with several research groups – most notably with Volodymyr Ivanovych Bezrodnyi at the Institute of Physics of the NAS of Ukraine – was a development of Oleksandr Ishchenko's ideas on laser materials based on organic dyes [16–18]. The first successful demonstration worldwide of passive mode-locking of Erbium-doped laser at 1340 nm represented a particularly notable achievement in this area [19].

The third – one in which I was fortunate to participate – involved fundamental studies on the solvatochromism, electronic structure, and photophysical properties of merocyanines [20, 21]. The success of this pursuit owed much to Oleksandr Oleksandrovych's deep understanding of the electronic structure of conjugated systems, extensive use of the method of moments for spectral data analysis (using the program he had developed), and the broad collaboration with physicist-spectroscopists that he established. This collaboration made it possible, in particular, to obtain essential spectral data at cryogenic temperatures [22, 23], to record for the first time the absorption spectra of merocyanines in the gas phase [24], and to trace how the molecular structure of merocyanines affects their (photo)isomerization behavior and excited-state lifetimes [25, 26].

■ Imparting Knowledge

Yet throughout his long and fruitful scientific career, Oleksandr Oleksandrovych's defining passion was his tireless desire to share knowledge – to ignite curiosity and a love of science in people's hearts, regardless of their age. Even as a university student, he organized and conducted classes and lectures for schoolchildren and helped prepare prospective university applicants. And he never abandoned this mission after graduation.

Since the early 1990s, already a young Doctor of Sciences, he developed and taught a lecture course on electronic spectroscopy at his alma mater, the Faculty of Chemistry of Taras Shevchenko National University of Kyiv. Remarkably, he initially did so voluntarily and was formally appointed to a professorship only in 1998. His lectures – clear and accessible, yet truly fundamental and richly illustrated with examples both from his own research and from the most up-to-date scientific achievements – attracted not only

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students but also graduate students and even faculty members.

This popularity stemmed not only from his natural teaching talent and ability to connect with an audience but also from his meticulous preparation of both content and visual materials. Both components were continuously refined, improved, and expanded from year to year. Later, to the course on electronic spectroscopy, he added an independently designed special course on materials science and on physical methods for the investigation of chemical compounds. In addition to the Faculty of Chemistry, Oleksandr Ishchenko also taught several courses at the Educational and Research Institute of High Technologies of the same university from its founding in 2009.

■ Concluding Remarks

To encompass an entire human life within the bounds of a memorial article is a task that goes far beyond what is possible. A globe may serve as an adequate model of the Earth, yet it still conceals more than it reveals. Our imagination and experience remind us that behind every genuine success, every achievement that remains in people's memory, lie immense effort – above all, the labor of self-discipline and self-development – as well as a deep love: love for one's chosen path, for knowledge, for people, and the courage to make difficult choices in difficult times.

The scientific career of Professor Oleksandr Ishchenko was far from an "easy walk." Within the Department of Color and Structure of Organic Compounds, he advanced from engineer to the head of the Department – a position he held from 2006 until his sudden passing on July 31, 2024. In 2015, he was elected a Corresponding Member, and in 2021, a Full Member of the National Academy of Sciences of Ukraine. Yet these marks of recognition and professional success also meant that he had less time for what he loved most – the search for new knowledge and the joy of sharing it.

He had many ideas and plans for future studies and projects. He lived, worked, and thought creatively to the very end.

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