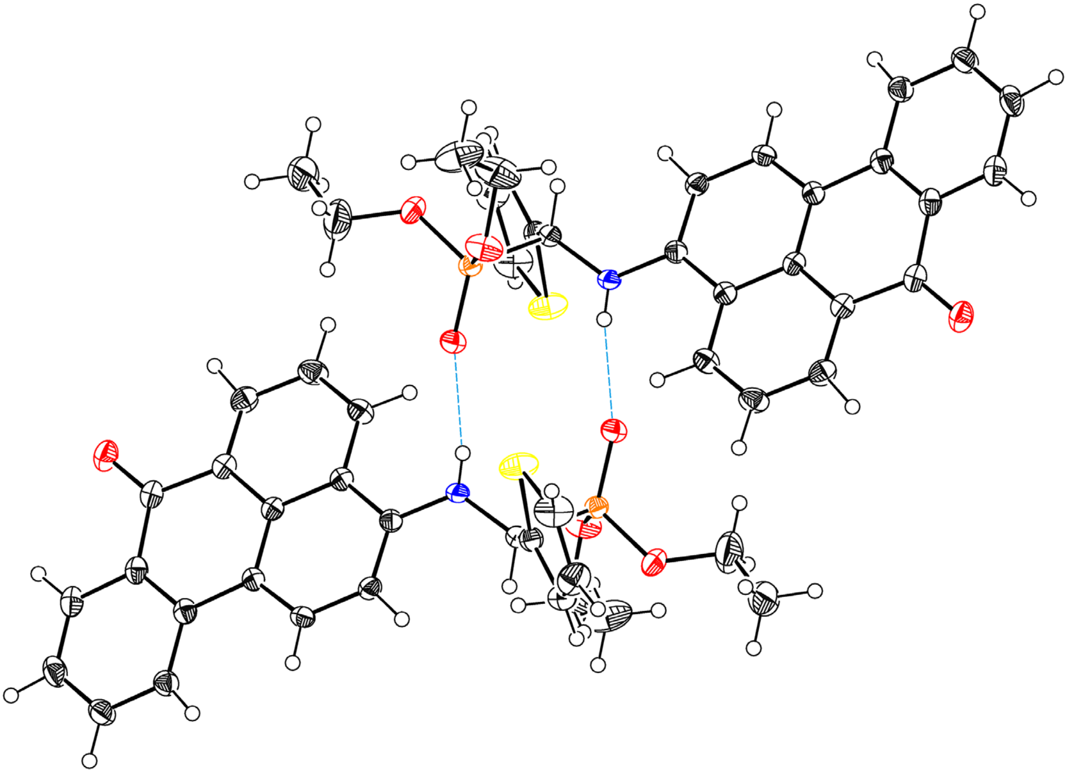
RIGA TECHNICAL UNIVERSITY

Armands Maļeckis

SYNTHESIS AND PROPERTIES OF NOVEL ANTHRONE FLUOROPHORES

Summary of the Doctoral Thesis



RTU Press
Riga 2025

RIGA TECHNICAL UNIVERSITY
Faculty of Natural Sciences and Technology
Institute of Chemistry and Chemical Technology

Armands Maļeckis
Doctoral Student of the Study Programme “Chemistry, Materials Science and Engineering”

SYNTHESIS AND PROPERTIES OF NOVEL ANTHRONE FLUOROPHORES

Summary of the Doctoral Thesis

Scientific supervisor
Docent, Senior Researcher Dr. chem. JEĻENA KIRILOVA

Consultant
Professor Dr. chem. MĀRIS TURKS

RTU Press
Riga 2025

Maļeckis, A. Synthesis and Properties of Novel Anthrone Fluorophores. Summary of the Doctoral Thesis. – Riga: RTU Press, 2025. – 39 p.

Published in accordance with the decision of the Promotion Council "RTU P-01" of 13 February 2025, Minutes No. 04030-9.1/67.

This work has been supported by the European Social Fund within Project No. 8.2.2.0/20/I/008, "Strengthening of PhD students and academic personnel of Riga Technical University and BA School of Business and Finance in the strategic fields of specialization" of the Specific Objective 8.2.2 "To Strengthen Academic Staff of Higher Education Institutions in Strategic Specialization Areas" of the Operational Programme "Growth and Employment" and by Riga Technical University's Doctoral Grant programme.

NATIONAL
DEVELOPMENT
PLAN 2020

EUROPEAN UNION
European Social
Fund

INVESTING IN YOUR FUTURE

Cover picture by Armands Maļeckis

https://doi.org/10.7250/9789934371684
ISBN 978-9934-37-168-4 (pdf)

DOCTORAL THESIS PROPOSED TO RIGA TECHNICAL UNIVERSITY FOR PROMOTION TO THE SCIENTIFIC DEGREE OF DOCTOR OF SCIENCE

To be granted the scientific degree of Doctor of Science (Ph. D.), the present Doctoral Thesis has been submitted for defence at the open meeting of RTU Promotion Council on 17 June 2025 at the Faculty of Natural Sciences and Technology of Riga Technical University, 3 Paula Valdena Street, Room 272 with online participation option at zoom link https://rtucloud1.zoom.us/j/9352086644.

OFFICIAL REVIEWERS

Senior Researcher Dr. chem. Aiva Plotniece
Latvian Institute of Organic Synthesis, Latvia

Corresponding member of the Latvian Academy of Sciences, Dr. chem. Māra Jure
Latvian Academy of Sciences, Latvia

Associate Professor Dr. chem. Artis Kinēns
University of Latvia, Latvia

DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for review to Riga Technical University for promotion to the scientific degree of Doctor of Science (Ph. D) is my own. I confirm that this Doctoral Thesis has not been submitted to any other university for promotion to a scientific degree.

Armands Maļeckis ……………………………. (signature)
Date: ………………………

The Doctoral Thesis has been prepared as a collection of thematically related scientific publications complemented by summaries in both Latvian and English. The Doctoral Thesis unites eight scientific publications. The scientific publications have been written in English, with a total volume of 328 pages, including supplementary data.

CONTENTS

GENERAL OVERVIEW OF THE THESIS

Introduction

Fluorescence occurs when a substance absorbs light and almost instantly reemits it at a longer wavelength, typically within a few nanoseconds. This reemitted light has less energy than the absorbed light, resulting in a shift to a longer wavelength. Excellent fluorescent materials are characterized by their unique optical properties: they have high absorption coefficients for effective excitation, significant Stokes shifts for increased sensitivity, high quantum yields for efficient light emission, and strong photostability for enduring performance. These properties are crucial for applications such as biological imaging, diagnostic assays and optical sensors, as the photodegradation process can produce undesirable by-products that may cause measurement errors and reduce the accuracy and reliability of results [1].

Among the myriad polyaromatic compounds, benzanthrones (7*H*-benzo[*de*]anthracen-7-ones) have long held a significant position in the dye industry due to their unique properties and versatile applications. These anthraquinoid dyes exhibit efficient charge transfer, facilitated by the interaction between electron-donating groups and the electron-accepting carbonyl group within the aromatic structure. This interaction is particularly pronounced in nitrogen-substituted derivatives. Consequently, 3-amino substituted benzanthrones have garnered considerable attention and have been the focus of extensive research owing to the strong electron-donating effects of nitrogen. For instance, nucleophilic substitution reactions involving 3-nitrobenzanthrone and 3-bromobenzanthrone with primary and secondary aliphatic amines produce substituted 3-aminobenzanthrones. Research indicates that these compounds are well-suited for the mass coloration of polymers and the production of liquid-crystal systems and exhibit nonlinear optical (NLO) properties [2]–[5]. Additionally, imines synthesized through the condensation reaction of 3-aminobenzanthrone with suitable aromatic aldehydes are effective for detecting various metal cationic species and can also be used in liquid crystal systems and polymers as fluorescent dyes and brighteners [6]–[9]. When these imines are reduced with $NaBH_4$, they yield amines that exhibit even more pronounced luminescence than the original imines [10], [11]. Acylation of 3-aminobenzanthrone with chloroacetyl chloride followed by nucleophilic substitution of the chlorine atom with amines yields tertiary or quaternary ammonium compounds, which are ideal for diverse sensing applications [12]–[14]. Similarly, amidino derivatives have been extensively studied, synthesized via the Vilsmeier–Haack type reaction [15]. These solvatochromic compounds are primarily used in confocal laser scanning microscopy (CLSM) for biological specimens [16], [17]. Aromatic substitution reactions of 3-bromobenzanthrone with alcohols produce fluorescent 3-oxybenzanthrones, which, like amines and imines, are suitable for polymer and liquid crystal systems [18]. The Buchwald-Hartwig amination of 3-bromobenzanthrone with aromatic amines such as phenoxazine and phenothiazine results in compounds emitting in the deep-red/near-infrared region with thermally activated delayed fluorescence properties, suitable for fabrication of devices with quantitative oxygen sensing capabilities in air [19]. Carbazole derivatives, on the other hand, exhibit self-regulating mechanochromism, adding to their versatility in various advanced applications [20].

In essence, the extensive exploration of benzanthrones and their derivatives not only underscores their potential role in various industries but also illuminates a promising avenue for advancing fluorescence technology and its multifaceted applications in fields ranging from materials science to biomedical research.

Aims and objectives

The aim of the Thesis was the synthesis of new benzanthrone and anthraquinone derivatives and the examination of their luminescent properties and potential applications.

The following tasks were defined:

1. to research methods for synthesizing novel benzanthrone and anthraquinone derivatives through nucleophilic aromatic substitution, Kabachnik-Fields and Sonogashira reactions, expanding the library of fluorescent compounds;
2. obtain absorption and emission spectra in various solvents and analyze molar extinction coefficients, Stokes shifts and fluorescence quantum yields of the obtained dyes to comprehensively examine photophysical properties;
3. based on the photophysical parameters, outline potential applications.

Scientific novelty and main results

Previous studies on benzanthrone derivatives have been mostly limited to the analysis of substituted 3-aminobenzanthrone derivatives. In this work, the impact of other heteroatoms, additional functional group introductions and elongation of conjugation on the properties of these compounds has been investigated, which up to this point has not been investigated.

The Doctoral Thesis encompasses, firstly, the synthesis of substituted 3-amino-9-nitrobenzanthrone derivatives, with a focus on understanding how additional electron-withdrawing groups influence molecular behavior during light absorption and emission processes. Additionally, the synthesis and properties of novel α-aminophosphonates derived from 1-aminoanthraquinone and 3-aminobenzanthrone were investigated in a comparative fashion, exploring their potential biological activities and photophysical behaviors. Furthermore, the research investigates the synthesis and properties of alkyl and aryl 3-thiobenzanthrones, shedding light on their luminescent properties and structural characteristics. Lastly, the synthesis and properties of 3-alkynylbenzanthrones, aiming to enhance their fluorescent characteristics, were explored.

Overall, the research contributes to the understanding of novel anthrone derivatives' structure-property relationships and their potential applications in such fields as bioimaging, nonlinear optics, and fluorescence-based technologies.

Structure and volume of the Thesis

The Doctoral Thesis has been prepared as a collection of thematically related scientific publications related to the functionalization and photophysical properties of benzanthrones and anthraquinones with applications in bioimaging. The Thesis unites six original research publications.

Publications and approbation of the Thesis

The results of the Thesis are reported in six original experimental publications. The main results were presented at international conferences.

Scientific publications

1. **Maļeckis, A.**; Griškjāns, E.; Cvetinska, M.; Savicka, M.; Belyakov, S.; Kirilova, E. Synthesis, Characterization, Spectroscopic Studies and Evaluation of Toxicological Effect on Growth of Wheat Sprouts (*Triticum Aestivum*) of New Benzanthrone α-Aryl-α-Aminophosphonates. *J. Mol. Struct.* **2023**, *1277*, 134838. https://doi.org/10.1016/j.molstruc.2022.134838.
2. **Maļeckis, A.**; Cvetinska, M.; Griškjāns, E.; Mežaraupe, L.; Kirjušina, M.; Pavlova, V.; Kirilova, E. Novel Anthraquinone α-Aryl-α-Aminophosphonates: Synthesis, Spectroscopy and Imaging by Confocal Laser Scanning Microscopy of Trematode *Opisthioglyphe Ranae*. *J. Photochem. Photobiol. A Chem.* **2023**, *444*, 114918. https://doi.org/10.1016/j.jphotochem.2023.114918.
3. **Maļeckis, A.**; Cvetinska, M.; Puckins, A.; Osipovs, S.; Sirokova, J.; Belyakov, S.; Kirilova, E. Synthesis and Properties of New 3-Heterylamino-Substituted 9-Nitrobenzanthrone Derivatives. *Molecules* **2023**, *28* (13), 5171. https://doi.org/10.3390/molecules28135171.
4. **Maļeckis, A.**; Cvetinska, M.; Griškjāns, E.; Dmitrijevs, K.; Traskovskis, K.; Belyakov, S.; Kirilova, E. Benzanthrone Sulfides: Synthesis, Solvatochromism Characterization and Analysis of Experimental Photophysical Parameters and Theoretical Calculations. *Dyes and Pigments* **2023**, *219*, 111599. https://doi.org/10.1016/j.dyepig.2023.111599.
5. **Maļeckis, A.**; Cvetinska, M.; Kirjušina, M.; Mežaraupe, L.; Kecko, S.; Gavarāne, I.; Kiyan, V.; Lider, L.; Pavlova, V.; Savicka, M.; Belyakov, S.; Kirilova, E. A Comparative Study of New Fluorescent Anthraquinone and Benzanthrone α-Aminophosphonates: Synthesis, Spectroscopy, Toxicology, X-Ray Crystallography, and Microscopy of *Opisthorchis Felineus*. *Molecules* **2024**, *29* (5), 1143. https://doi.org/10.3390/molecules29051143.
6. **Maļeckis, A.**; Cvetinska, M.; Griškjāns, E.; Kirilova, E. Exploring Dual Solvatochromic Traits in Novel Fluorescent Benzanthrone Ethynyl Derivatives. *J. Solution. Chem.* **2024**. https://doi.org/10.1007/s10953-024-01363-x.

Other publications on the topic not included in the Doctoral Thesis

1. **Maļeckis, A.**; Griškjāns, E.; Cvetinska, M.; Kirilova, E. 3-(Phenylethynyl)-7H-Benzo[de]Anthracen-7-one. Molbank 2022, *2022* (3), M1442. https://doi.org/10.3390/M1442.
2. Olipova, M.; **Maleckis, A.**; Puckins, A.; Kirilova, A.; Romanovska, E.; Kirilova, E. Spectroscopic Investigation of New Benzanthrone Luminescent Dyes. *Bulgarian Chemical Communications* **2022**, *54* (3), 253–257. https://doi.org/10.34049/bcc.54.3.F006.

The results of the Thesis were presented at the following conferences

1. Kirilova, J.; **Maleckis, A.**; Puckins, A.; Kirilova, A.; Grigorjeva, T. (2022). Spectroscopic Investigation of New Benzanthrone Luminescent Dyes. *8th International Conference on New Trends in Chemistry,* Istanbul, Turkey, pp. 57. https://icntcconference.com/wp-content/uploads/2024/06/ICNTC-2022-ABSTRACT-BOOK.pdf
2. Sirokova, J.; **Maleckis, A.**; Kirilova, J. (2023). Effect of the Nitro Group on Nucleophilic Substitution in Benzanthrone. *The 65th International Scientific Conference of Daugavpils University*, Daugavpils, Latvia, p. 21. https://dukonference.lv/files/Tezes_65.konf_publicesanai_gala_versija.pdf
3. **Maļeckis, A.**; Griškjāns, E.; Cvetinska, M.; Kirilova, E. (2023). Synthesis and Examination of Photophysical Properties of Benzanthrone Ethynyl Derivatives. *The 65th International Scientific Conference of Daugavpils University*, Daugavpils, Latvia, p. 23. https://dukonference.lv/files/Tezes_65.konf_publicesanai_gala_versija.pdf
4. Kirilova, J.; Savicka, M.; Kirilova, A.; **Maleckis, A.**; Grigorjeva, T. (2023). Study of the Toxicity of Benzanthrone Luminescent Dyes. *9th International Conference On New Trends in Chemistry*, Istanbul, Turkey, p. 43. https://icntcconference.com/wp-content/uploads/2024/06/9th-ICNTC-BOOK-OF-ABSTRACTS.pdf
5. **Maļeckis, A.**; Kirilova, E. (2024). Advancements in Fluorescent α-aminophosphonates. *The 66th International Scientific Conference of Daugavpils University*, Daugavpils, Latvia, p. 13. https://dukonference.lv/files/Tezes_66_konf_2024_gala.pdf

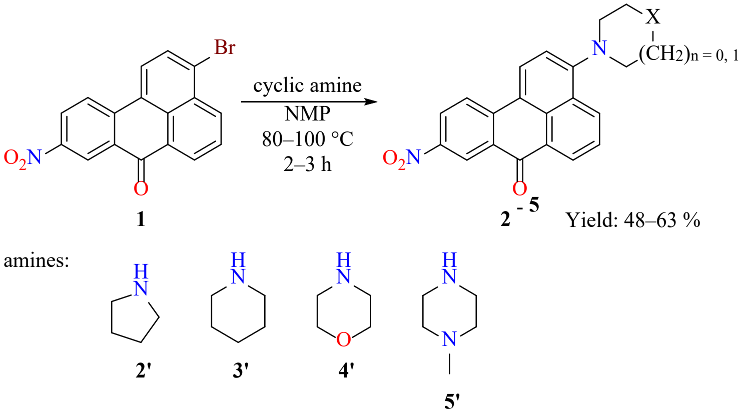
MAIN RESULTS OF THE THESIS

Anthrone derivatives have gained prominence for their remarkable luminescent attributes and tunable fluorescence emission, which enable diverse applications. Recognizing their potential, recent years have seen a surge in research focused on the synthesis and functionalization of anthrone derivatives. This growing interest stems from the need to explore new molecular structures with enhanced optical properties and tailor-made functionalities to meet the demands of evolving technological and scientific challenges. Consequently, further investigation was required to elucidate the structure-property relationships of anthrone derivatives and devise efficient synthetic strategies to expand their applicability further to unlock the full potential of anthrone derivatives and drive innovation in fluorescent materials science.

In this Thesis, the primary objective centered on the synthesis of new benzanthrone and anthraquinone fluorophores, accompanied by comprehensive measurements of the photophysical properties and the determination of their potential applications.

1. Synthesis and properties of substituted 3-amino-9-nitrobenzanthrone derivatives

The fluorescence observed in benzanthrone dyes primarily occurs due to intramolecular charge transfer (ICT) taking place upon excitation. This happens due to the interaction between electron-donating groups and the electron-accepting carbonyl group within the aromatic system of benzanthrone (D-π-A architecture type). Noteworthy, substituted 3-aminobenzanthrone derivatives display nonlinear optical properties [21]; with the addition of a nitro group notably augmenting their NLO (nonlinear optical) response [22], therefore, it was of interest to investigate the impact of an additional electron-withdrawing group on photophysical attributes of substituted 3-aminobenzanthrone derivatives of benzanthrone.



Scheme 1. Synthesis of substituted 3-amino-9-nitrobenzanthrone derivatives **2**–**5**.

For this objective, commercial 3-bromobenzanthrone was nitrated with a nitrating mixture (HNO_3/H_2SO_4 (4:1 v/v)) in glacial acetic acid, according to a previously published study, to obtain compound **1** via an electrophilic substitution reaction [23], which then underwent following nucleophilic aromatic substitution with cyclic amines in 1-methylpyrrolidin-2-one (NMP) as depicted in Scheme 1. Compared to the corresponding substitution reaction involving non-nitrated 3-bromobenzanthrone, the substitution of the bromine atom in nitro derivative **1** occurs at a lower temperature (80–100 °C versus 86–138 °C) and more rapidly (2–3 hours versus 8 hours). The enhanced reactivity stems from the potent electron-withdrawing character of the nitro group, leading to a significant reduction in electron density at the *C*(3) atom of the benzanthrone core, promoting the nucleophilic attack. Consequently, the yields of the desired products **2**–**5** were, on average, 10 % higher compared to equivalent derivatives lacking a nitro group [2]. These resulting compounds are dark red colored in their solid state and display intense luminescence in solutions.

While structures of these compounds were confirmed and characterized by Fourier transform infrared spectroscopy (FTIR), ^{1}H, ^{13}C nuclear magnetic resonance (NMR) spectroscopy and 2D-NMR (COSY and HSQC) spectroscopy and high-resolution mass spectrometry, in addition, slow evaporation technique provided crystals of **2** and **3**. X-ray crystallographic analysis, besides providing clear confirmation of the structures, also unveiled the presence of hydrogen bonds for both compounds and π–π interactions leading to molecular stacking (Figs. 1 and 2). The X-ray crystallographic analysis for all compounds mentioned in this work was carried out in collaboration with Dr. sc. phys. Sergey Belyakov.

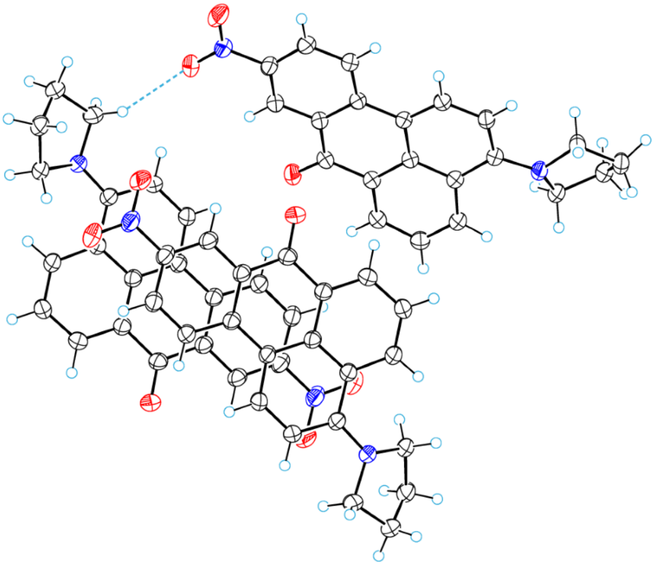


Fig. 1. A fragment of molecular packing of **2** with N–O···H–C hydrogen bonds.

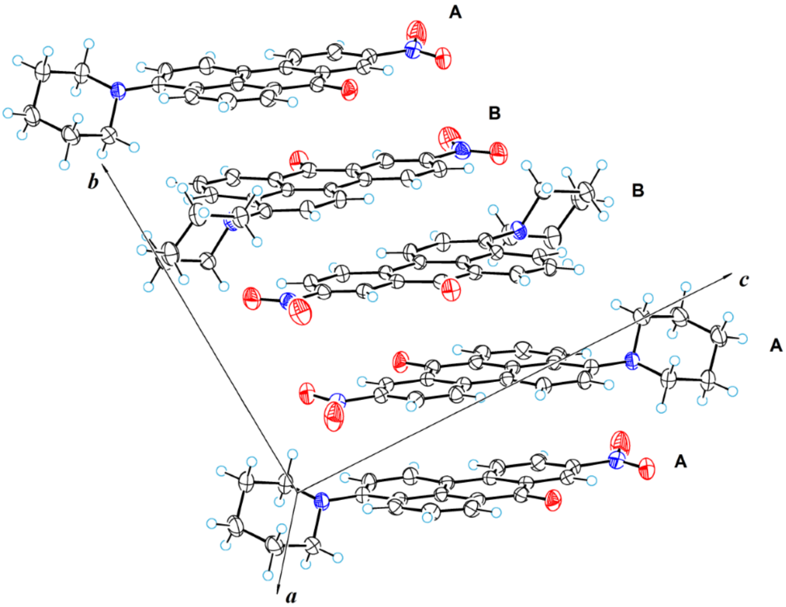


Fig. 2. A perspective view of the molecular stack of compound **3**.

The obtained dyes exhibit remarkable luminescent characteristics in different organic solvents. In this connection, the photophysical properties of the synthesized derivatives were examined, acquiring the absorption and emission spectra in seven organic solvents (benzene, ethyl acetate (EtOAc), chloroform ($CHCl_3$), acetone, ethanol (EtOH), *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO)) with a vast selection of polarities. The obtained spectral data are summarized in Tables 1 and 2, and Fig. 3 visually represents ultraviolet-visible (UV-Vis) absorption and fluorescence emission spectra of compound **3** in various organic solvents.

Table 1

Values of empirical polarity solvent parameter $E_T(30)$ [24]; absorption maxima and logarithmic value of molar absorption coefficient of compounds **2**–**5** in organic solvents (concentration 10^{-5} M)

Solvent	$E_T(30)$	Absorption λ_{abs}, nm; (lgε)			
		2	**3**	**4**	**5**
Benzene	34.3	498 (3.94)	460 (4.55)	447 (4.47)	453 (4.26)
EtOAc	38.1	493 (3.92)	459 (4.53)	447 (4.49)	454 (4.15)
$CHCl_3$	39.1	505 (4.01)	474 (4.62)	449 (4.56)	462 (4.26)
Acetone	42.2	512 (4.08)	467 (4.51)	448 (4.60)	462 (4.11)
EtOH	51.9	526 (3.97)	471 (4.50)	449 (4.49)	455 (3.99)
DMF	43.2	519 (4.18)	475 (4.50)	460 (4.54)	467 (4.17)
DMSO	45.1	531 (4.06)	478 (4.49)	466 (4.43)	472 (4.11)

Table 2

Fluorescence maxima and Stokes shifts of compounds **2**–**5** in organic solvents (concentration 10^{-5} M)

Solvent	Emission λ_{em}, nm, and Stokes shift, cm^{-1}							
	2		**3**		**4**		**5**	
Benzene	584	2957	578	4438	570	4564	574	4653
CHCl$_3$	613	3489	606	4596	592	4827	598	4923
EtOAc	598	3562	598	5064	592	5380	592	5135
Acetone	621	3428	620	5284	612	5479	612	5305
EtOH	661	3882	661	6103	652	5981	645	6474
DMF	630	3395	632	5230	624	6935	622	5336
DMSO	641	3231	643	5368	650	5713	634	5413

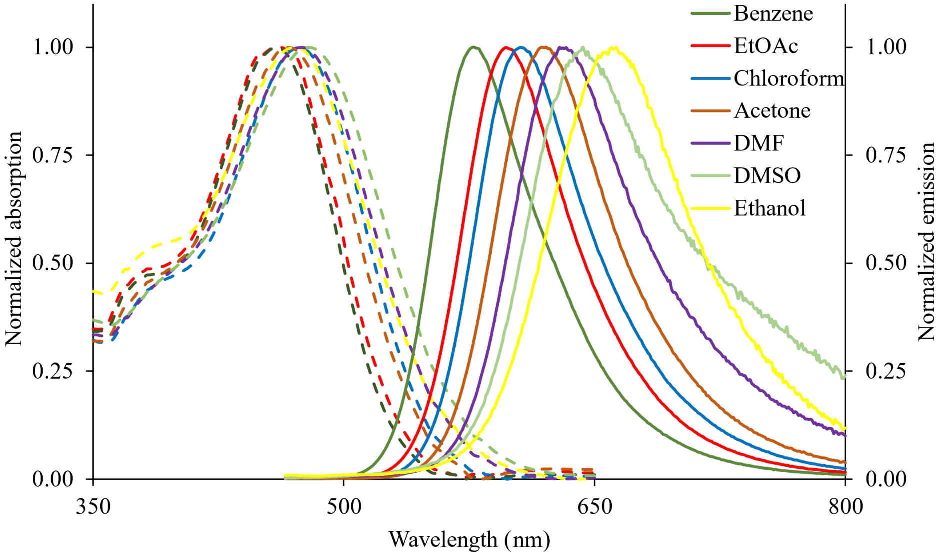


Fig. 3. Normalized UV-Vis absorption and fluorescence emission spectra of compound **3** in various organic solvents.

Derivative **2** absorbs light at 498–531 nm and exhibits a bathochromic shift of 33 nm from nonpolar benzene to polar DMSO, while amines **3** and **5** have shorter wavelength absorption band at 453–478 nm and shorter bathochromic shift of 18–19 nm.

The non-nitrated pyrrolidine derivative obtained earlier demonstrates absorption in the most extensive wavelength spectrum (525–558 nm) compared to all other compounds examined [3]. In the case of the prior, stronger interaction between the donor and the acceptor groups leads to a lowered electronic transition energy and an increase in the charge transfer once the photon is absorbed. The hypsochromic shift of the absorption band of compound **2** and the reduced sensitivity of the absorption maxima to the solvent polarity suggest a decrease in the ICT nature of the electronic transition. Thus, incorporating an electronegative nitro group into the molecule leads to competition between this substituent and the molecule's carbonyl group, resulting in a new electron density distribution in the ground state.

In comparison to non-nitrated amines, compounds **2**–**5** exhibit stronger absorption; the average lgε is 4.30 for compounds **2**–**5**, whereas it is around 4.19 for non-nitrated counterpart compounds. The bathochromic shift of luminescence maxima (from benzene to DMSO) of the synthesized derivatives is similar to the bathochromic shift of non-nitrated derivatives: 60–85 nm.

Nitrated compounds **2** and **3** exhibit a shift in absorption maxima towards longer wavelengths, ranging from 15 nm to 35 nm, compared to their non-nitrated counterparts. However, their emission maxima display a shift towards shorter wavelengths, ranging from 3 nm to 14 nm, in comparison to the luminescence spectra of monosubstituted derivatives. Consequently, the Stokes shifts of the spectra of nitro derivatives are reduced compared to those of non-nitrated derivatives.

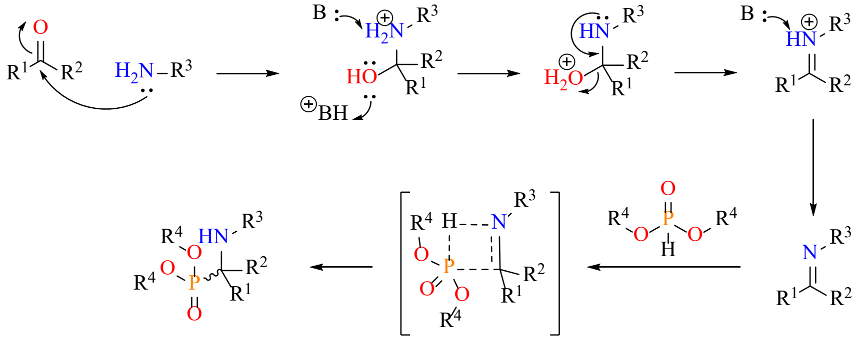
2. Synthesis and properties of α-aminophosphonates derived from 3-aminobenzanthrone

α-Aminophosphonates are analogous to amino acids (N-C-PO_3H_2 and N-C-CO_2H structural fragments accordingly) and thus possess a variety of biological activities due to their ability to inhibit enzymes involved in the metabolism of amino acids – acting as antagonists [25]. Thus, novel α-aminophosphonates are studied as potential antibiotics [26], antifungal [27] and chemotherapeutic agents [28], herbicides [29] and neuromodulators [30]. Additionally, these compounds have the potential to be used as antioxidants [31], sorbents [32], [33], corrosion inhibitors [34] and lubricating additives [35].

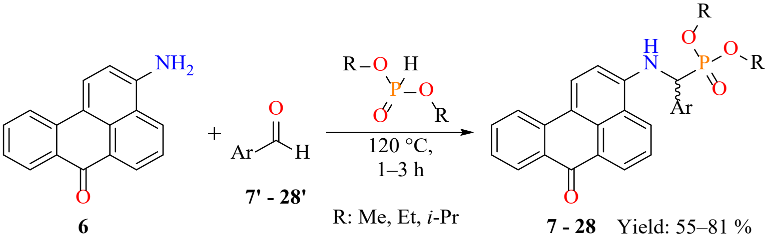
While many derivatives of α-aminophosphonates were obtained for diverse purposes, up to now, such fluorescent compounds have been scarcely studied, and the research is limited to benzene, naphthalene, anthracene and pyrene derivatives [36]–[40].

With the above mentioned in mind, it was concluded to be worth synthesizing and investigating the properties of 3-aminobenzanthrone α-aryl-α-aminophosphonate derivatives.

Synthetically α-aminophosphonates are usually obtained through Kabachnik-Fields reaction. This is a tricomponent coupling reaction of a carbonyl compound – a ketone or an aldehyde, an amine and a phosphonate (also referred to as a phosphite) (Scheme 2). Several modifications of this reaction were introduced since the discovery of this synthetic approach; among these are catalyzed variations, uncatalyzed ones and those employing dehydrating agents, ionic liquids and microwave irradiation [41]. Firstly, starting compound **6** was synthesized by reduction of 3-nitrobenzanthrone with sodium sulfide, which in turn was obtained by nitration of commercially available benzanthrone as described in previous research [42]. Then, it was decided on the most convenient and efficient method – a one-pot catalyst and solvent free one, where dialkyl phosphonate acts as a reactant and as a solvent. At 120 °C, the reaction yields orange to red compounds in 55–81% yield (Scheme 3). Thus, 22 compounds were obtained –a small library (Table 3), resulting from the investigation of both the nature of the aromatic substituent (with electron-accepting and electron-donating groups in various positions on the benzene ring and other types of substituents, such as 2-thienyl derivatives) on the alpha carbon, and the influence of phosphonate group substituents (methyl, ethyl, and isopropyl) on the properties of the new benzanthrone fluorophores.



Scheme 2. Proposed mechanism of the Kabachnik-Fields reaction [43].



Scheme 3. Synthesis of benzanthrone α-aminophosphonate derivatives **7**–**28**.

Table 3

Structures of the obtained compounds **7**–**28**

R \ Ar	C_6H_5-	C_6H_4-(4-Me)	C_6H_4-(4-F)	C_6H_4-(4-Cl)	C_6H_4-(4-Br)	C_6H_4-(4-SMe)	C_6H_4-(4-OMe)	C_6H_4-(2-OMe)	C_6H_3-(3-CN-4-F)	2-thienyl
Me	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Et	**17**	**18**	**19**	**20**	–	–	–	**21**	–	**22**
i-Pr	**23**	**24**	**25**	–	–	–	**26**	**27**	–	**28**

FTIR, ^{1}H-, ^{13}C- and ^{31}P-NMR spectra and mass spectrometric analysis confirm the chemical structures of prepared compounds. The X-ray crystallographic study of benzanthrone α-aminophosphonates additionally provided insights into the molecular arrangement and intermolecular interactions of these compounds in the crystalline state (Figs. 4–7). All molecular structures possess an asymmetric carbon atom, yet their crystal structures are achiral, therefore, these compounds represent true racemates. In the crystal structure of compound **17**, strong π-π stacking interactions occur between benzanthrone systems. In contrast, both compounds **22** and **23** exhibit strong intermolecular bonds of NH···O type in their crystal structure. Notably, the molecular structure of compound **11** features a strong intramolecular NH···O hydrogen bond between the amino group and the dimethyl phosphonate, forming an additional five-membered ring.

Absorbance and emission spectra of compounds **7**–**17** and **23** were acquired in solvents of varying polarity to investigate the photophysical properties of the obtained compounds. All the examined dyes exhibited fluorescence and displayed significant solvatochromic behavior, emitting light ranging from green in hexane to red in ethanol. No notable impact of substituents on the phenyl group or the type of aromatic substituent on the α-carbon (phenyl or thienyl), nor of phosphonate alkyl groups (methyl, ethyl, or isopropyl), was observed on the photophysical characteristics of the resulting chromophores. The first exception is the slightly elevated molar attenuation coefficients (4.60 (benzene) and 4.65 (DMSO)) observed in compound **23**, which bears bulkier isopropyl groups, in contrast to compounds **7** (4.10 (benzene) and 4.08 (DMSO)) and **17** (4.05 (benzene) and 4.03 (DMSO)), indicating a more pronounced absorption of electromagnetic radiation. The second one is compound **15**, which bears strong electron-accepting groups, which decrease the extinction coefficients and quantum yields. Using compound **11** as an example, it is noted that benzanthrone α-aminophosphonates in solutions display a wide-band absorbance approximately between 458 nm and 500 nm and fluoresce from 534 nm (in hexane) to 636 nm (in ethanol) (Fig. 8), resulting in bathochromic shifts of 42 nm and 102 nm, respectively. This indicates that the polarity effect of the medium on fluorescence is more pronounced than on absorption. The highest Stokes shift among the examined dyes, measuring 4963 cm^{-1}, was noted for compound **16** in ethanol. The absorption spectra of previously investigated benzanthrone amidines fall within the range of 410 nm to 495 nm [15], [44], having absorption in the shorter wavelength region. In contrast, 3-substituted benzanthrone amino derivatives demonstrate absorption in the range of 430 nm to 520 nm [2], [10], having absorption in the longer wavelength region. It appears that the benzanthrone amino group, when attached to a phosphoryl group (compounds **7**–**28**), exhibits a donating effect slightly weaker than that of an alkyl amino group yet stronger than an amidino group.

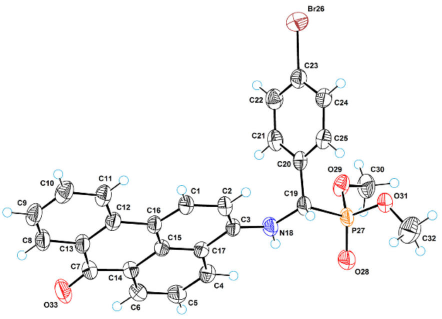


Fig. 4. ORTEP diagram of **11**. Crystal system: monoclinic.

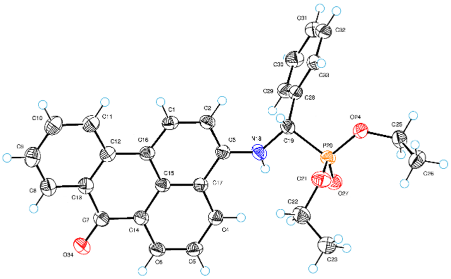
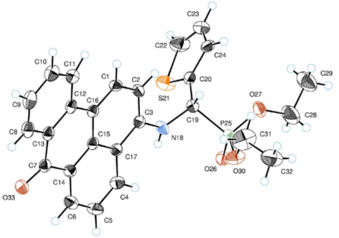


Fig. 5. ORTEP diagram of **17**. Crystal system: orthorhombic.



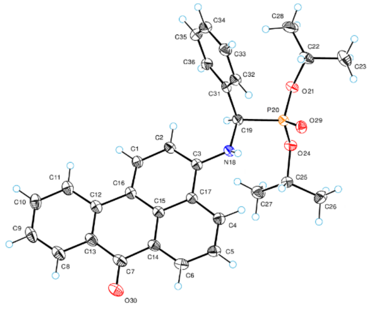


Fig. 6. ORTEP diagram of **22**. Crystal system: monoclinic.

Fig. 7. ORTEP diagram of **23**. Crystal system: triclinic.

.

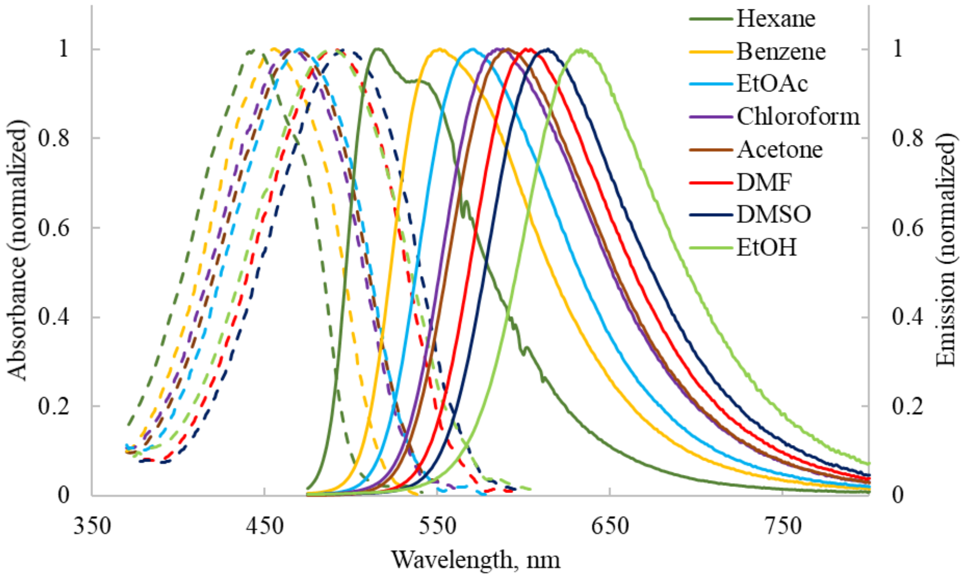


Fig. 8. Normalized UV-Vis absorption and fluorescence emission spectra of compound **11** in various organic solvents.

Using polarity-sensitive luminescent dyes is becoming more efficient in staining biological species in confocal laser scanning microscopy. Benzanthrone dyes **12** and **15,** enhanced by attached phosphoryl group lipophilicity, were utilized to bioimage the trematode *Opisthorchis felineus*, a parasite that mainly infects the livers of different mammals, including humans (Fig. 9) [45].

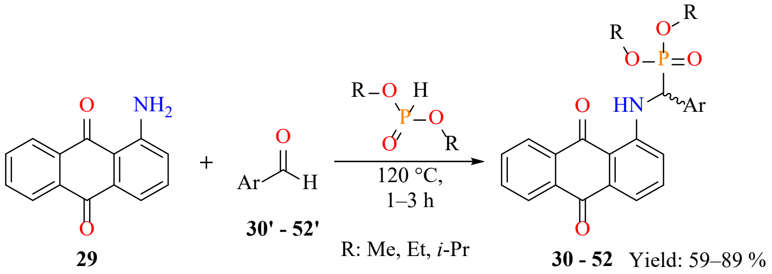
Fig. 9. Adult *Opisthorchis felineus* stained with the examined dyes: A – **12**;B – **15**.

To evaluate the toxicity of the obtained compounds and the impact of the aromatic substituent on the α-carbon atom, experiments were conducted on wheat sprout morphology, electrolyte leakage, malondialdehyde levels, and pigment quantification. Compounds with identical phosphonate group substituents (R = Me) and various aromatic groups (Ar) were used: a phenyl group without substituents (**7**), a phenyl group with a halogen atom, bromine, in the para position (**11**), and a thienyl group (**16**). Overall, benzanthrone α-aminophosphonates exhibit varying levels of toxic effects – phytotoxicity ranges from 37 % (**7**) to 83 % (**16**), depending on the concentration and the aromatic substituent on the α-carbon atom. The staining and toxicology of parasitic species were carried out in collaboration with researchers from the Institute of Life Sciences and Technology at Daugavpils University.

Thermal stability determines whether a compound can withstand the temperature conditions required for practical use over the long term. This was examined on the example of compound **17**, using differential thermal analysis (DTA) and thermogravimetry (TG) methods. According to the TG curve, thermal degradation occurs in two primary phases: between 270–330 °C (resulting in around 20 wt. % loss) and 630–950 °C (resulting in approximately 30 wt. % loss). Overall, the compound under analysis exhibits thermal stability up to roughly 270 °C, experiencing a 5 wt. % loss in initial mass, showing stability comparable to benzanthrone amino derivatives studied previously. To evaluate the impact of substituents on the thermal stability of the compounds, it would be worthwhile to continue the study.

3. Synthesis and properties of α-aminophosphonates derived from 1-aminoanthraquinone

Considering the scarcity of research on fluorescent α-aminophosphonate derivatives, a decision was made to take a step further and synthesize derivatives of anthraquinone for comparison with analogous benzanthrone compounds. Anthraquinone compounds are widely studied for use as fluorescent sensors [46], emitters and cell imaging agents [47], [48]. Some anthraquinone derivatives possess medicinal properties, including antibiotic, antiparasitic, insecticidal, fungicidal, and antiviral activities; they can also be used as chemotherapeutic agents [49], [50]. No anthraquinone α-aminophosphonates have been synthesized yet. The synthesis (Scheme 4) was carried out under the same conditions as for benzanthrones (Chapter 2). The structures of synthesized compounds are summarized in Table 4.



Scheme 4. Synthesis of anthraquinone α-aminophosphonate derivatives **30–52**.

Table 4

Structures of the obtained compounds **30–52**

Ar R	C_6H_5-	C_6H_4-(4-Me)	C_6H_4-(4-F)	C_6H_4-(4-Cl)	C_6H_4-(4-Br)	C_6H_4-(4-SMe)	C_6H_4-(4-OMe)	C_6H_4-(2-OMe)	C_6H_3-(3-CN-4-F)	2-thienyl
Me	**30**	**31**	**32**	**33**	**34**	**35**	**36**	**37**	**38**	**39**
Et	**40**	**41**	**42**	**43**	–	–	**44**	**45**	–	–
i-Pr	**46**	**47**	**48**	**49**	–	–	**50**	**51**	–	**52**

It is observed that in solutions, anthraquinone α-aryl-α-aminophosphonates exhibit broad band absorbance with maxima at around 465–488 nm showing small bathochromic shift from benzene to DMSO solution (5–8 nm) in contrast to unsubstituted compound **29**, for which the bathochromic shift of the absorption maximum between solutions in hexane and ethanol is 30 nm. Studied compounds show fluorescence with maxima from 585 nm (EtOAc) to 628 nm (DMSO), attaining fluorescence bathochromic shifts of up to 30 nm. The polarity effect of the medium on fluorescence is much more pronounced than on the absorption. It may be concluded that the impact of solvent polarity on the absorption and emission wavelength maxima is more pronounced for benzanthrone compounds. It is also observed that fluorescence quantum yields are higher for the analogous benzanthrone compounds **11**, **12** and **15** (0.10–0.57) compared to the anthraquinone derivatives **34**, **35** and **38** (< 0.01–0.14).

To gain a deeper understanding of the photostability of new dyes, the photofading behavior of the derived compounds was assessed in ethanol (at a concentration of 10^{-4} M). To determine the effect of the phosphonate group substituent R on the photostability of the compounds, an experiment was conducted with compounds containing methyl (**30**), ethyl (**40**) and isopropyl groups (**46**) and the same aromatic substituent (phenyl group) on the α-carbon atom. The results were compared with the photostability of the starting material, 1-aminoanthraquinone (**29**), and the widely used test dye fluorescein (FL) (Fig. 11). Following a 4-hour irradiation period, fluorescein retained 71 % of its initial absorbance, whereas compound **30** retained only 27 %. Among the obtained compounds, those with ethyl (**40**) and isopropyl (**46**) groups displayed the highest photostability, with a decrease in absorption of 40 %. These findings indicate that the synthesized dyes exhibit greater photostability compared to the unsubstituted amine **29**.

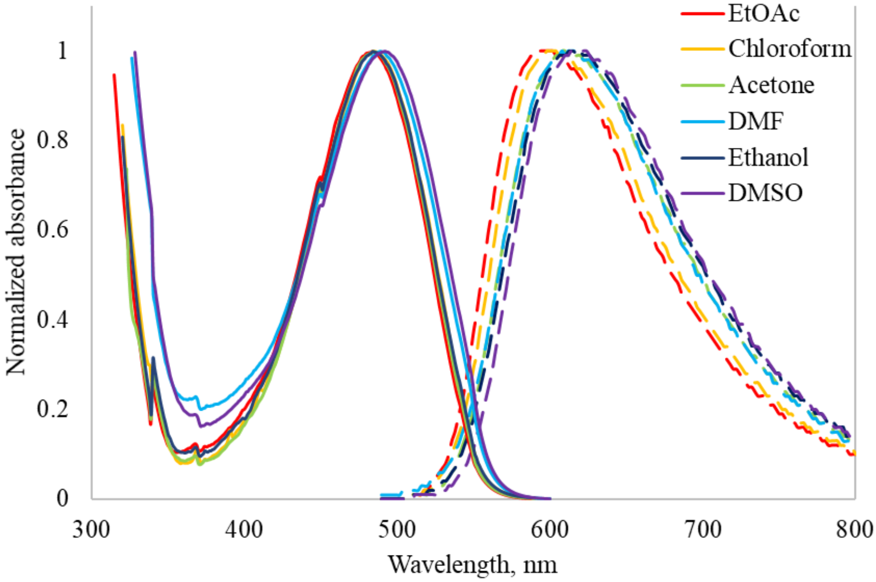


Fig. 10. Normalized UV-Vis absorption and fluorescence emission spectra of compound **49** in various organic solvents.

Anthraquinone α-aryl-α-aminophosphonates with an electron-donating group on benzene ring (4-thiomethyl) **35** and strong electron-withdrawing groups (3-cyano-4-fluoro) **38** were also subjected to testing for *Opisthorchis felineus*. Based on the initial data, benzanthrone dyes **12** and **15** with the same substituents, respectively, provided slightly clearer visualization of the structure and musculature of the parasite (Fig. 12). Consequently, it can be inferred that benzanthrone dyes **12** and **15** are more effective for visualizing *Opisthorchis felineus* flukes than anthraquinone dyes **35** and **38**. This can be attributed to a more lipophilic nature of the latter, which has a significant impact on the visualization of these biological objects. Dye **49** was also used to stain a common parasite of the Eurasian amphibians – *Opisthioglyphe ranae* (Fig. 13) [51]. Overall, all tested dyes – **12**, **15**, **35**, **38** and **49** – demonstrated promising initial outcomes and are applicable for detailed and rapid bioimaging.

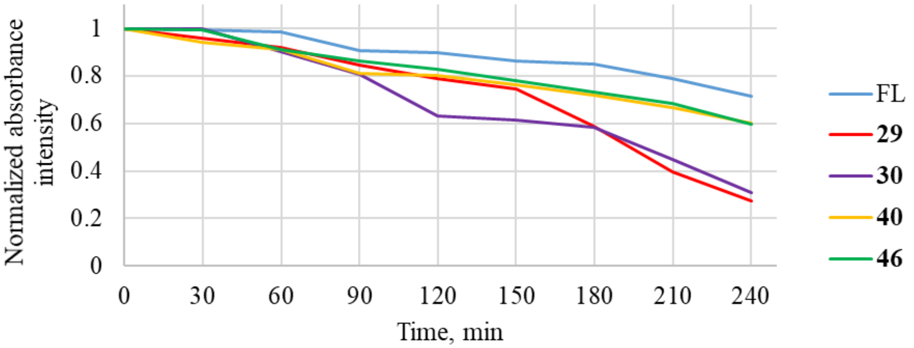


Fig. 11. Normalized absorbance intensities as a function of irradiation time upon 365 nm of fluoresceine (FL) and compounds **29**, **30**, **40** and **46**.

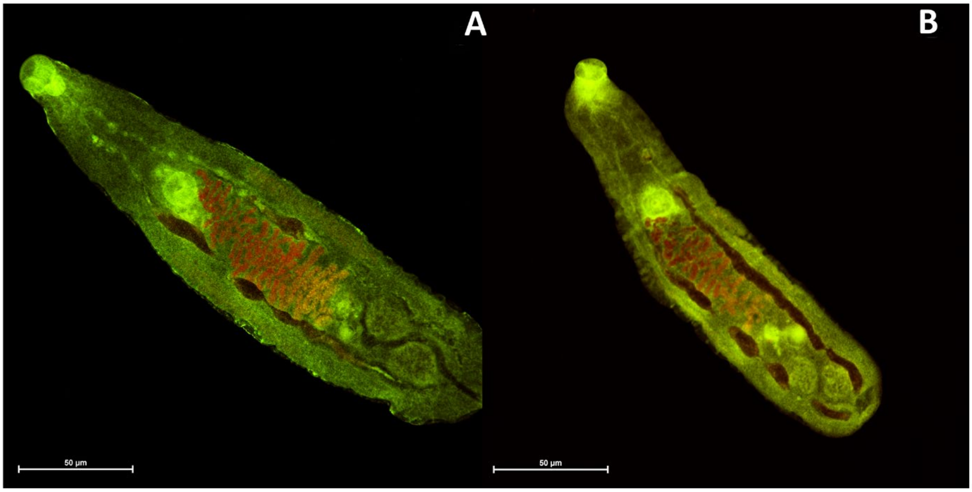


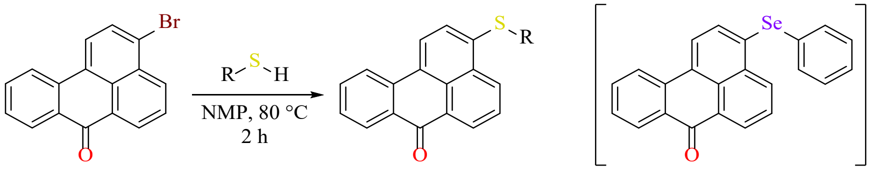
Fig. 12. Adult *Opisthorchis felineus* stained with the examined dyes: A – **35**;B – **38**.

Fig. 13. Adult *Opisthioglyphe ranae* stained with examined dye **49**.

4. Synthesis and properties of 3-thiobenzanthrones

To achieve the objective of the study, following the analysis of the properties of nitrogen-containing anthrone derivatives, the research was continued by introducing other heteroatoms into the benzanthrone molecule. Sulfur-containing compounds have garnered considerable attention within the scientific community. Notably, recent research has focused on various derivatives, including pyrene sulfides and sulfoxides [52], compounds featuring the dithiafulvene moiety [53], 1,5-bis-(4-alkylphenylthio)anthraquinone dyes with potential applications in liquid crystal systems [54], [55], as well as triarylcyclopentadiene compounds incorporating thiophene rings and dibenzothiophene groups [56]. These and other related compounds, along with their diverse applications, have been comprehensively reviewed in a recently published paper [57]. Previously, 3-mercaptobenzanthrone had been documented [58], and 14*H*-anthra[2,1,9-*mna*]thioxanthen-14-one was investigated as a semiconducting compound [59]. Additionally, benzanthrone compounds based on phenothiazine with thermally activated delayed fluorescence have been discussed [19]. Benzanthrone compounds featuring electron-donating substituents such as nitrogen and oxygen have been recorded and demonstrated to exhibit remarkable luminescent properties [18]. However, due to limited available data concerning thioalkyl and thiophenyl derivatives of benzanthrone, we have opted to pursue the synthesis and analysis of benzanthrone compounds incorporating sulfur and selenium.

Previously, numerous review articles extensively discussed the mechanism and synthesis of aliphatic and aromatic sulfides via nucleophilic aromatic substitution reactions [60]–[62]. This study introduces a practical approach to synthesize benzanthrone sulfides **54–62** (Table 5) through nucleophilic aromatic substitution reactions, utilizing 3-bromobenzanthrone as the principal electrophile and aliphatic thiols with varying steric bulk and aromatic thiols with electron-donating and electron-accepting groups as nucleophiles.



53 **54 - 62** Yield: 59–86 % **63** Yield: 60 %

Scheme 5. Synthesis of benzanthrone thio-derivatives **54–62** and structure of phenylselanyl derivative **63**.

Table 5

Summary of the structures of the obtained compounds **54–62**.

R	Me	*i*-Pr	cyclohexyl	*t*-Bu	-$(CH_2)_2$-Ph	C_6H_5-	C_6H_4-(4-Me)	C_6H_4-(4-F)	C_6H_4-(4-OMe)
Nr.	**54**	**55**	**56**	**57**	**58**	**59**	**60**	**61**	**62**

The reactions were conducted under basic conditions (NaOH) in *N*-methyl-2-pyrrolidone (NMP) (Scheme 5). Additionally, 3-(phenylselanyl)-7*H*-benzo[*de*]anthracen-7-one (**63**) was synthesized using the same method as aliphatic and aromatic sulfides, starting from sodium benzeneselenolate without the presence of a base, following a previously reported procedure. Theoretically, aliphatic thiols with larger steric bulk would be less reactive due to steric hindrance; in the case of aromatic thiols, those with electron-donating groups would be expected to exhibit greater reactivity due to increased nucleophilicity than those with electron-accepting groups [63], but a correlation between structures of substrates and reactivity has not been found.

FTIR, ^{1}H- and ^{13}C-NMR spectra and high-resolution mass spectrometric analysis confirmed the chemical structures of newly prepared compounds. Like in the crystal structures of 3-aminobenzanthrones, in the case of **15**, there also are π-π stacking interactions between benzanthrone systems and hydrogen bonds (Fig. 14).

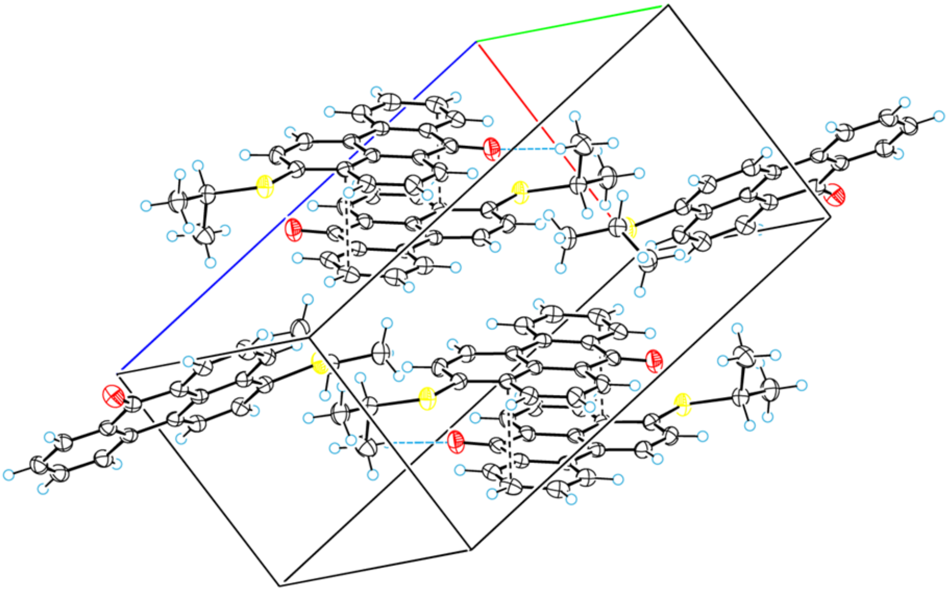


Fig. 14. Molecular packing in the unit cell of **55** showing the intermolecular shortened contacts.

Table 6 outlines the photophysical parameters of the thio derivatives with an aliphatic substituent (R = Me) **54** and an aromatic substituent (R = C_6H_5-) **59**, as well as 3-(phenylselanyl)benzanthrone **63**. The benzanthrone alkyl and aryl sulfides, along with 3-(phenylselanyl)benzanthrone in solutions, exhibited absorption bands ranging from 403 nm to 448 nm, with a shift towards longer wavelengths of 10 nm to 20 nm between the maxima in benzene and DMSO. Both alkyl and aryl sulfides emit light upon excitation from approximately

507 nm in benzene to 591 nm in ethanol (Fig. 15). Substituting the sulfur atom with the larger selenium atom slightly shifts the emission bathochromically and increases the Stokes shifts to some extent while extinction coefficients and absorption maxima remain largely unchanged. The highest fluorescence quantum yield for all studied compounds was observed in chloroform. Specifically, 3-(methylthio)benzanthrone exhibited the highest emission yield (0.31–0.52), followed by 3-(phenylthio)benzanthrone with slightly lower yields (0.08–0.24), while 3-(phenylselanyl)benzanthrone had the lowest emission yield (0.001–0.07). This trend is likely to be due to decreasing efficiency of charge transfer in the sequence.

Table 6

Absorption maxima and logarithmic value of molar absorption coefficient, fluorescence maxima, Stokes shifts, fluorescence quantum yields (Φ_F) and fluorescence lifetime values (τ) of compounds **54**, **59** and **63** in organic solvents (concentration 10^{-5} M)

Nr.	Solvent	Absorption λ_{abs}, nm; (lgε)	Emission λ_{em}, nm	Stokes shift, cm^{-1}	Φ_F	τ, ns
54	Benzene	429 (4.18)	508	3625	0.31	3.5
	$CHCl_3$	444 (4.16)	533	3761	0.52	10.0
	DMF	446 (4.06)	552	4306	0.40	10.7
	EtOH	448 (4.15)	587	5286	0.32	10.6
59	Benzene	413 (4.16)	504	4372	0.08	2.3
	$CHCl_3$	421 (4.18)	538	5166	0.24	9.3
	DMF	417 (4.15)	541	5497	0.14	5.6
	EtOH	423 (4.09)	583	6488	0.11	7.1
63	Benzene	416 (4.14)	510	4431	0.05	1.0
	$CHCl_3$	423 (4.14)	543	5224	0.07	3.7
	DMF	419 (4.11)	562	6073	0.001	-[a]
	EtOH	423 (4.04)	595	6834	0.001	-[a]

[a] The value could not be determined due to the low intensity of fluorescence.

Previously analyzed benzanthrone amidines absorb at 410–495 nm [15], [44], while 3-substituted benzanthrone amino derivatives absorb at 430–520 nm [2], [10]. As for the 3-methoxy and 3-phenoxy derivatives of benzanthrone, their absorption spectra range from 417 nm to 436 nm [18]. Interestingly, in sulfur and selenium derivatives, both the peaks of emission and absorption shift towards shorter wavelengths, indicating a slightly weaker donating effect compared to nitrogen and oxygen-containing species, which is also confirmed by the Hammett substituent constants, where the value for the amino group (-NH_2) is −0.66, −0.37 for the hydroxyl group (-OH), −0.10 for the thiol group (-SH), and −0.05 for the selenol group (-SeH) [64]. The ICT character and the nanosecond-scale light emission process of the dyes are indicative of the fluorescence emission mechanism.

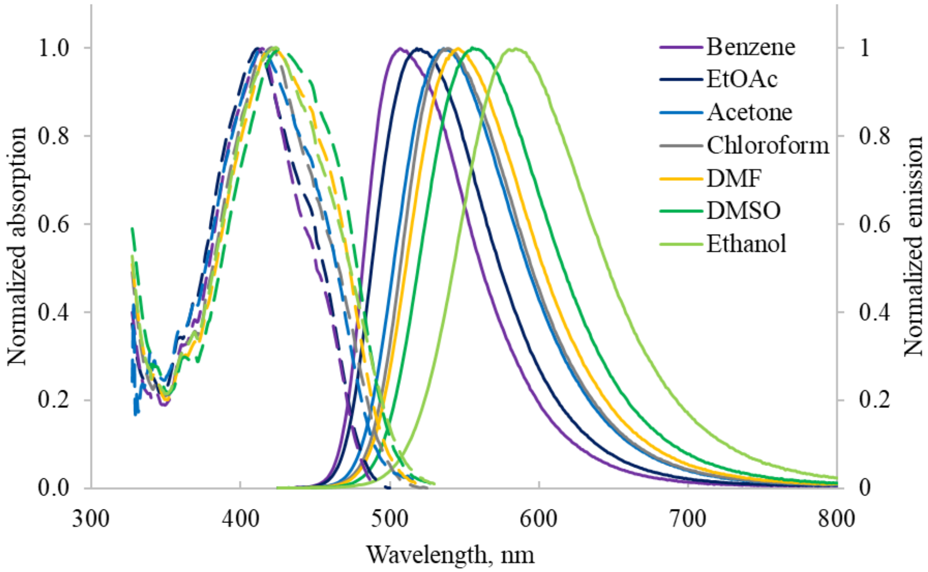


Fig. 15. Normalized UV-Vis absorption and fluorescence emission spectra of compound **59** in various organic solvents.

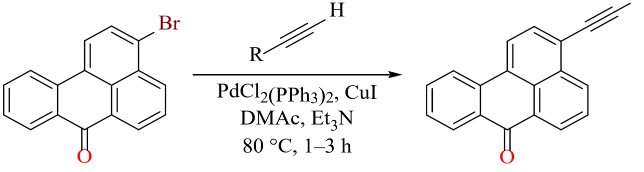
5. Synthesis and properties of 3-alkynylbenzanthrones

Another approach to fluorophore modification, in addition to the previously discussed methods of introducing functional groups and heteroatoms, is the extension of the conjugated system within the molecule.

Several theoretical and practical investigations indicate that directly attaching phenylacetylene groups to luminescent molecules alters their photophysical properties, enhancing fluorescent characteristics and enabling various applications. These molecules encompass pyrene [65], carbazole [66], anthraquinone [67], naphthalimide [68], and quninolylthiazole [69]. Such compounds can be applied in sensor technologies, organic light-emitting diode production, and fluorescent labeling [70]–[72]. Moreover, studies suggest that introducing electron-donating or electron-withdrawing groups to the phenyl rings of phenylacetylene moieties and adjusting the π-conjugation length can modify fluorescence yields, Stokes shift sizes, and absorption and emission maxima [73]. Consequently, it was determined to undertake the investigation of previously unexplored benzanthrone alkynes.

As of now, within the realm of palladium-catalyzed reactions, the only documented methods for synthesizing novel derivatives of benzanthrone are aryl cyanation and Buchwald–Hartwig amination reactions [19], [74]. The Sonogashira reaction is a cross-coupling reaction employed for synthesizing alkynes. It entails the reaction of a terminal alkyne with a palladium catalyst, a copper(I) co-catalyst, and an aryl (or vinyl) halide [75]. These conditions were utilized for synthesizing compounds **64**–**68** (Table 7) from 3-bromobenzanthrone (**53**) in *N*,*N*-dimethylacetamide, with triethylamine serving as a base (Scheme 6). The reaction progresses through a sequence of stages, commencing with the oxidative addition of the palladium catalyst to the aryl or vinyl halide, leading to the reductive elimination of the desired alkyne product. The copper(I) co-catalyst is crucial for facilitating the transmetalation step [76]. To determine the effect of the nature of the substituent R on the properties of the compounds, synthesis was carried out using terminal alkynes with electron-donating and electron-withdrawing groups of varying strength.

In the Sonogashira reaction, the products are formed through the creation of a new C-C bond between two covalent ligands as a result of reductive elimination. It is known that reductive elimination occurs slower in electron-rich complexes than in electron-deficient ones [77]. Consequently, higher reaction yields could be expected with alkynes containing electron-withdrawing groups; however, no correlation was found between the substrate structures and the reaction yields.



53 **64 - 69** Yield: 43–89 %

Scheme 6. Synthesis of benzanthrone alkynyl-derivatives **64**–**69**.

Table 7

Summary of the structures of the obtained compounds **64**–**69**

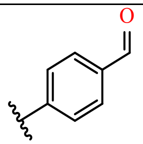
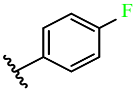
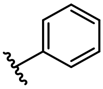
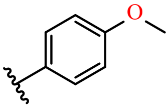
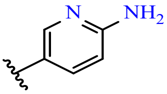
R						
Nr.	**64**	**65**	**66**	**67**	**68**	**69**

Table 8

Absorption maxima and logarithmic value of molar absorption coefficient of compounds **64**–**69** in organic solvents (concentration 10^{-5} M)

Solvent	Absorption λ_{abs}, nm; (lgε)				
	64	**65**	**67**	**68**	**69**
Benzene	416 (4.65)	423 (4.55)	427 (4.51)	432 (4.32)	423 (4.24)
EtOAc	412 (4.68)	416 (4.56)	425 (4.51)	437 (4.29)	419 (4.29)
$CHCl_3$	420 (4.72)	425 (4.52)	436 (4.46)	438 (4.49)	427 (4.22)
Acetone	414 (4.65)	419 (4.55)	432 (4.49)	445 (4.41)	419 (4.27)
DMF	419 (4.71)	423 (4.58)	437 (4.48)	455 (4.54)	422 (4.25)
DMSO	422 (4.68)	435 (4.50)	440 (4.42)	462 (4.55)	424 (4.26)
EtOH	430 (4.25)	429 (4.57)	442 (4.45)	446 (4.36)	419 (4.19)

Table 9

Fluorescence maxima and Stokes shifts of compounds **64**–**69** in organic solvents (concentration 10^{-5} M)

Solvent	Emission λ_{em}, nm, and Stokes shift, cm^{-1}				
	64	**65**	**67**	**68**	**69**
Benzene	463 (2440)	466 (2181)	502 (3499)	530 (4280)	482 (2894)
$CHCl_3$	462 (2627)	473 (2897)	510 (3922)	576 (5522)	479 (2990)
EtOAc	479 (2933)	498 (3449)	534 (4209)	574 (5409)	491 (3053)
Acetone	475 (3102)	492 (3541)	565 (5449)	641 (6871)	488 (3375)
DMF	481 (3076)	497 (3520)	553 (4800)	691 (7506)	495 (3495)
DMSO	489 (3247)	506 (3226)	570 (5183)	720 (7756)	494 (3342)
EtOH	515 (3838)	531 (4478)	598 (5902)	701 (8156)	495 (3664)

All investigated dyes exhibit fluorescence and demonstrate a significant solvatochromic effect (Tables 8 and 9). Figure 16 represents UV-Vis absorption and fluorescence emission spectra of compound **66** in various organic solvents. In solutions, benzanthrone alkynes exhibit two absorption bands around 310–330 nm and 420–450 nm, showing a bathochromic shift of 12–30 nm for the long wavelength absorption band between the maxima in benzene and DMSO. The impact of the polarity of solvents on fluorescence is more prominent than on absorbance. Synthesized compounds are fluorescent with emission from 462 nm (**64**, EtOAc) to 701 nm (**68**, EtOH). Obtained compounds display dual solvatochromism – not only emission peak of each individual compound is influenced by solvent polarity, but a strong correlation between the electronic nature of substituents and photophysical parameters is evident as well; electron-withdrawing substituents shift emission hypsochromically and strong electron-donating substituents – bathochromically in the same solvent (Fig. 17). The electronic properties of the substituents significantly influence the emission efficiency of the studied substances. Derivatives with electron-withdrawing groups (**64** and **65**) have a higher luminescence quantum yield in ethanol (0.67 and 0.74, respectively) compared with less polar solvents (0.01–0.41). In contrast, derivatives with donor groups luminesce more intensely in chloroform than in ethanol. In turn, the presence of a trimethylsilyl group leads to a dramatic drop in emission efficiency. The alteration of photophysical parameters also has an impact on Stokes shifts. Specifically, the range of Stokes shifts varies from 2181 cm^{-1} for compound **65** in a less polar solvent (benzene) to 8156 cm^{-1} for compound **68** in a polar ethanol. Thus, the presence of an electron-donating substituent leads to a larger Stokes shift.

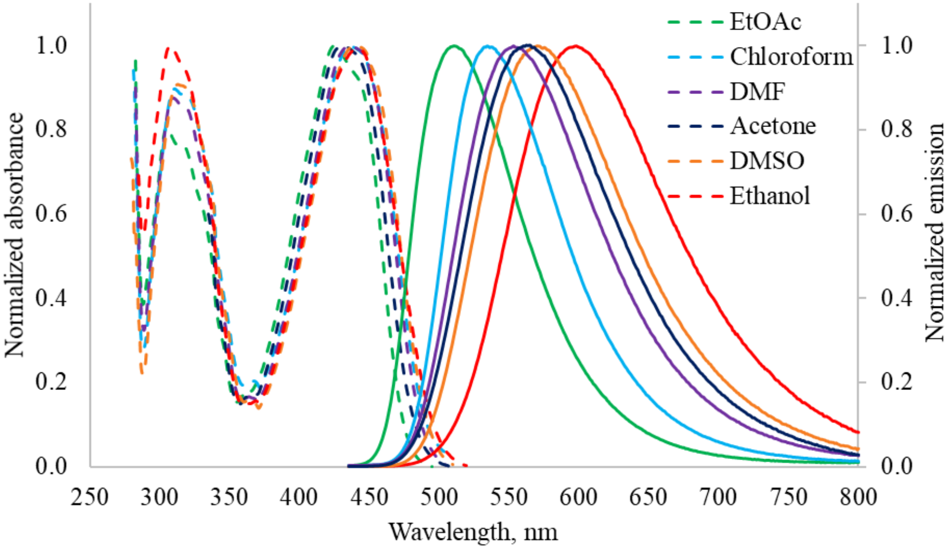


Fig. 16. Normalized UV-Vis absorption and fluorescence emission spectra of compound **66** in various organic solvents.

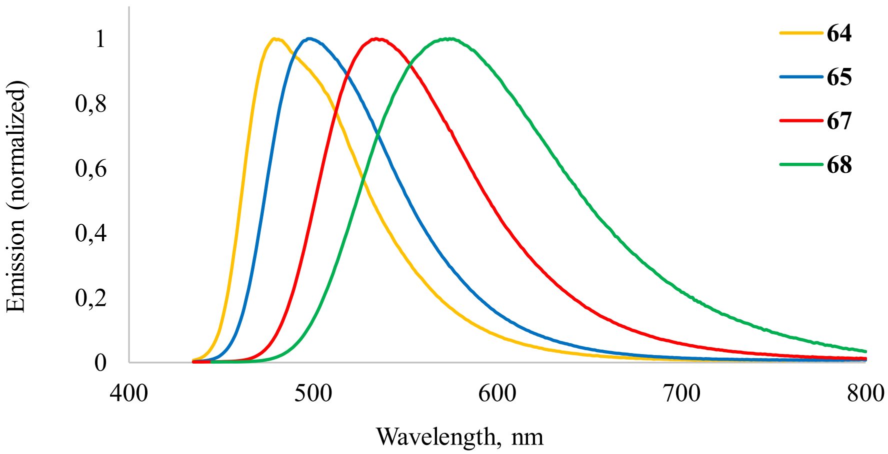


Fig. 17. Normalized fluorescence emission spectra of compounds **64**–**67** in chloroform.

To estimate the photostability of the dyes **64**–**69**, the photofading process of synthesized derivatives was conducted in ethanol (at a concentration of 10^{-4} M) and compared with the widely used test dye, fluorescein. The results are illustrated in Fig. 18. Following a 4-hour irradiation period, fluorescein exhibited an absorbance of 71 % of its initial level. Among the synthesized compounds, derivative **65** with a fluorine atom displayed the highest photostability, retaining 96 % of its initial absorption. Following closely is compound **64**, featuring a formyl group with a photostability of 82 %. Conversely, the derivative containing a methoxy group, compound **67**, demonstrated the lowest stability, losing more than half of its absorption (57 %) by the end of the experiment. These findings indicate that three of the synthesized substances – **64**, **65**, and **69** – exhibit greater photostability than fluorescein.

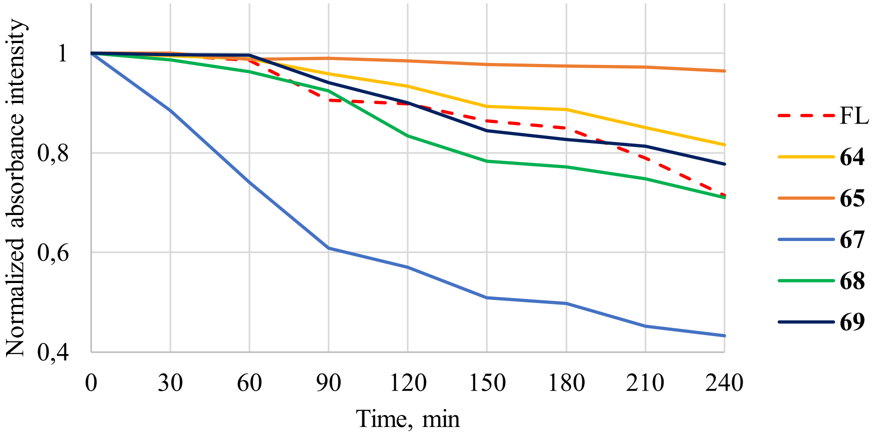


Fig. 18. Normalized absorbance intensities as a function of irradiation time upon 365 nm of fluoresceine (FL) and compounds **64**–**68**.

Given the established nonlinear optical properties of certain benzanthrones and the understanding that extending π-conjugation may enhance these properties, both these benzanthrone alkynes and compounds not covered in the Thesis, specifically, products obtained in reaction with 4-ethynyl-*N*,*N*-dimethylaniline, 1-ethynyl-4-(trifluoromethyl)benzene, 3-ethynylthiophene and methyl propiolate, are currently being investigated for their nonlinear optical characteristics.

As a result of the work, the collection of fluorescent compounds of benzanthrone and anthraquinone was expanded. The Stokes shift dependence on the absorption maximum in acetone for the compounds studied in the Thesis is shown in Fig. 19. Benzanthrone and anthraquinone amino derivatives exhibit longer wavelength absorption and emission, allowing them to be used in microscopy for staining biological objects, as this reduces sample autofluorescence and achieves increased image contrast. Thioalkyl and thiophenyl substituents have a weaker electron-donating effect, which increases the required energy for the benzanthrone's excited state. Although benzanthrone thio derivatives generally have larger Stokes shifts (from 4089 cm^{-1} to 6052 cm^{-1}) than α-aminophosphonates (from 3798 cm^{-1} to 4170 cm^{-1}), their emission wavelength is too short for effective application in confocal laser scanning microscopy. Additionally, for benzanthrone alkyne derivatives, the absorption and emission maxima increase with the enhancement of the substituent's electron-donating effect; however, in contrast to other compounds, as the absorption maximum increases, the Stokes shift also increases. For example, compound **(64)** with a strong electron-withdrawing substituent absorbs light with a maximum at 414 nm, and its Stokes shift is 3102 cm^{-1}. In contrast, compound (**68**) with a strong electron-donating substituent absorbs light with a maximum at 445 nm, and its Stokes shift is 6871 cm^{-1}. In order to reasonably establish the nature of these relationships, further research is needed.

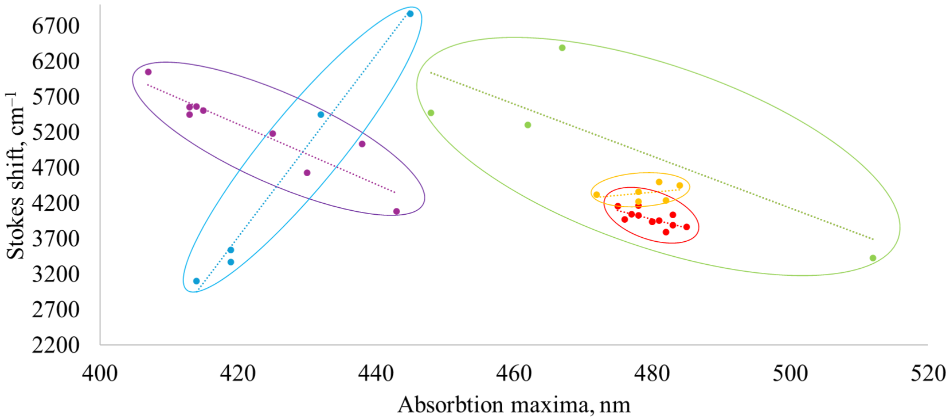
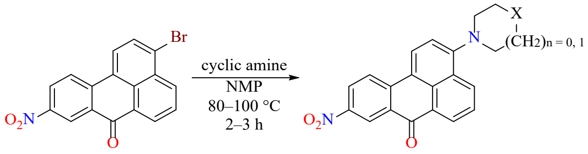


Fig. 19. The dependence of the Stokes shift of the compounds studied in this work on the absorption maximum in acetone. Green: benzanthrone 3-amino-9-nitro derivatives; red: benzanthrone α-aminophosphonates; orange: anthraquinone α-aminophosphonates; purple: benzanthrone thio derivatives; blue: benzanthrone alkynyl derivatives.

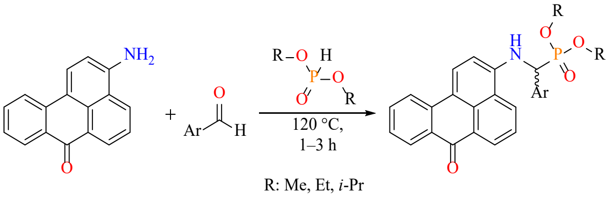
CONCLUSIONS

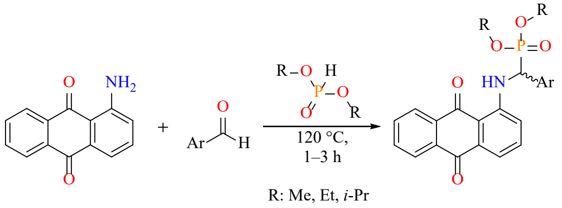
1. As a result of the research, new synthesis methods for benzanthrone and anthraquinone derivatives were successfully investigated. The range of fluorescent compounds was expanded with derivatives obtained through nucleophilic aromatic substitution, Kabachnik-Fields, and Sonogashira reactions. Spectral analysis was performed on the obtained compounds, and their photophysical properties were studied. Additionally, the practical application of the new compounds with enhanced properties in microscopy was demonstrated.

2. Aromatic substitution reaction of 3-bromo-9-nitrobenzanthrone provides substituted 3-amino-9-nitrobenzanthrones in 48–63 % yield with absorption from 447 nm to 531 nm and emit light from 570 nm to 650 nm. The reactivity of 3-bromo-9-nitrobenzanhtrone is enhanced compared to non-nitrated analogues, and higher molar absorption coefficients render them better candidates for non-linear optics.



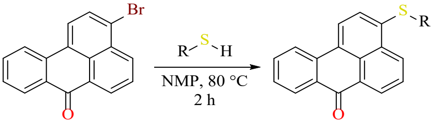
3. Kabachnik-Fields reaction of 3-aminobenzanthrone and 1-aminoanthraquinone provides fluorescent α-aminophosphonates in 55–89 % yield. The emission band shows a bathochromic shift from hexane to DMSO; for benzanthrone derivatives, it reaches 100 nm, while for anthraquinone, it is only 40 nm. Fluorescence quantum yields of benzanthrone α-aminophosphonates are up to 10 times higher, from 0.01 to 0.17 for anthraquinone derivatives and from 0.1 to 0.56 for benzanthrone derivatives.



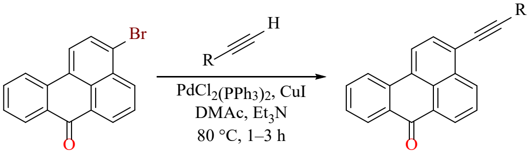


4. Both benzanthrone and anthraquinone α-aminophosphonates (compounds **12**, **15**, **35**, **38**, and **49**) are suitable for staining and studying biological samples, particularly parasitic trematodes, using confocal laser scanning microscopy.

5. Aromatic substitution reaction of 3-bromobenzanthrone with thiols provides alkyl and aryl substituted 3-thiobenzanthrone dyes in 59–86 % yield. Studied compounds exhibit fluorescence and solvatochromism with quantum yields of up to 52 %, absorption from 403 nm to 448 nm and emit light from 507 nm to 591 nm.



6. Sonogashira reaction of 3-bromobenzanthrone with terminal alkynes was studied. This reaction provides substituted 3-alkynylbenzanthrones in 43–89 % yield with 420–450 nm long-wave absorption and emits light from 462 nm to 701 nm. Electron-donating groups on aryl rings of alkynes shift absorption and emission maxima bathochromically, whereas electron-withdrawing groups – hypsochromically. High photostability and elongated π-conjugation make them possible candidates for applications in non-linear optical technologies.



REFERENCES

1. Introduction to Fluorescence. In *Principles of Fluorescence Spectroscopy*; Springer US: Boston, MA, 2006; pp. 1–26.
2. Grabchev, I.; Bojinov, V.; Moneva, I. The Synthesis and Application of Fluorescent Dyes Based on 3-Amino Benzanthrone. *Dyes and Pigments* **2001**, *48*, 143–150, doi:10.1016/S0143-7208(00)00098-X.
3. Kirilova, E. M.; Meirovics, I.; Belyakov, S. V. Preparation and Properties of Nitrogen Derivatives of Benzanthrone with Heterocyclic Fragments. *Chem. Heterocycl. Compd. (N Y)* **2002**, *38*, 789–792, doi:10.1023/A:1020621418164.
4. Siddlingeshwar, B.; Hanagodimath, S. M.; Kirilova, E. M.; Kirilov, G. K. Photophysical Characteristics of Three Novel Benzanthrone Derivatives: Experimental and Theoretical Estimation of Dipole Moments. *J. Quant. Spectrosc. Radiat. Transf.* **2011**, *112*, 448–456, doi:10.1016/j.jqsrt.2010.09.001.
5. Thomas, A.; Kirilova, E. M.; Nagesh, B. V.; Manohara, S. R.; Siddlingeshwar, B.; Belyakov, S. V. Synthesis, Solvatochromism and DFT Study of Pyridine Substituted Benzanthrone with ICT Characteristics. *J. Mol. Struct.* **2022**, *1262*, 132971, doi:10.1016/j.molstruc.2022.132971.
6. Grabchev, I.; Moneva, I. Synthesis and Properties of Benzanthrone Derivatives as Luminophore Dyes for Liquid Crystals. *Dyes and Pigments.* **1998**, *37*, 155–164, doi:10.1016/S0143-7208(97)00050-8.
7. Grabtchev, I. K.; Bojinov, V. B.; Moneva, I. T. Functional Properties of Azomethine Substituted Benzanthrone Dyes for Use in Nematic Liquid Crystals. *J. Mol. Struct.* **1998**, *471*, 19–25, doi:10.1016/S0022-2860(98)00400-1.
8. Grabchev, I.; Mykowska, E.; Moneva, I.; Bauman, D. Molecular Orientation of Some Fluorescent Dichroic Dyes in Nematic Liquid Crystal. *Zeitschrift für Naturforschung A.* **2004**, *59*, 368–374, doi:10.1515/zna-2004-0610.
9. Almalki, A. S. A.; Alhadhrami, A.; Obaid, R. J.; Alsharif, M. A.; Adam, A. M. A.; Grabchev, I.; Refat, M. S. Preparation of Some Compounds and Study Their Thermal Stability for Use in Dye Sensitized Solar Cells. *J. Mol. Liq.* **2018**, *261*, 565–582, doi:10.1016/j.molliq.2018.04.057.
10. Orlova, N.; Nikolajeva, I.; Pučkins, A.; Belyakov, S.; Kirilova, E. Heterocyclic Schiff Bases of 3-Aminobenzanthrone and Their Reduced Analogues: Synthesis, Properties and Spectroscopy. *Molecules.* **2021**, *26*, 2570, doi:10.3390/molecules26092570.
11. Kirilova, A.; Pučkins, A.; Belyakov, S.; Kirilova, E. 3-[N-(4-Methoxybenzyl)Amino]Benzo[de]Anthracen-7-One. *Molbank.* **2021**, *2021*, M1287, doi:10.3390/M1287.
12. Staneva, D.; Betcheva, R. Synthesis and Functional Properties of New Optical PH Sensor Based on Benzo[de]Anthracen-7-One Immobilized on the Viscose. *Dyes and Pigments.* **2007**, *74*, 148–153, doi:10.1016/j.dyepig.2006.01.029.
13. Staneva, D.; Grabchev, I. Heterogeneous Sensors for Ammonia, Amines and Metal Ions Based on a Dendrimer Modified Fluorescent Viscose Fabric. *Dyes and Pigments.* **2018**, *155*, 164–170, doi:10.1016/j.dyepig.2018.03.044.
14. Staneva, D.; Vasileva-Tonkova, E.; Makki, M. S. I.; Sobahi, T. R.; Abdel-Rahman, R. M.; Asiri, A. M.; Grabchev, I. Synthesis, Photophysical and Antimicrobial Activity of New Water Soluble Ammonium Quaternary Benzanthrone in Solution and in

Polylactide Film. *J. Photochem. Photobiol. B.* **2015**, *143*, 44–51, doi:10.1016/j.jphotobiol.2014.12.024.

15. Gonta, S.; Utinans, M.; Kirilov, G.; Belyakov, S.; Ivanova, I.; Fleisher, M.; Savenkov, V.; Kirilova, E. Fluorescent Substituted Amidines of Benzanthrone: Synthesis, Spectroscopy and Quantum Chemical Calculations. *Spectrochim Acta A Mol. Biomol. Spectrosc.* **2013**, *101*, 325–334, doi:10.1016/j.saa.2012.09.104.
16. Kirilova, E.; Kecko, S.; Mežaraupe, L.; Gavarāne, I.; Pučkins, A.; Mickeviča, I.; Rubeniņa, I.; Osipovs, S.; Bulanovs, A.; Pupiņš, M.; et al. Novel Luminescent Dyes for Confocal Laser Scanning Microscopy Used in Trematoda Parasite Diagnostics. *Acta Biochim. Pol.* **2018**, *65*, 449–454, doi:10.18388/abp.2018_2574.
17. Rubenina, I.; Gavarane, I.; Kirilova, E.; Mezaraupe, L.; Kirjusina, M. Comparison of the Benzanthrone Luminophores: They Are Not Equal for Rapid Examination of Parafasciolopsis Fasciolaemorpha (Trematoda: Digenea). *Biomolecules.* **2021**, *11*, 598, doi:10.3390/biom11040598.
18. Grabchev, I.; Moneva, I.; Wolarz, E.; Bauman, D. Fluorescent 3-Oxy Benzanthrone Dyes in Liquid Crystalline Media. *Dyes and Pigments.* **2003**, *58*, 1–6, doi:10.1016/S0143-7208(03)00033-0.
19. Tsiko, U.; Bezvikonnyi, O.; Volyniuk, D.; Minaev, B. F.; Keruckas, J.; Cekaviciute, M.; Jatautiene, E.; Andruleviciene, V.; Dabuliene, A.; Grazulevicius, J.V. TADF Quenching Properties of Phenothiazine or Phenoxazine-Substituted Benzanthrones Emitting in Deep-Red/near-Infrared Region towards Oxygen Sensing. *Dyes and Pigments.* **2022**, *197*, 109952, doi:10.1016/j.dyepig.2021.109952.
20. Tsiko, U.; Sych, G.; Volyniuk, D.; Bezvikonnyi, O.; Keruckiene, R.; Lazauskas, A.; Grazulevicius, J. V. Self-Recovering Mechanochromic Luminescence of the Derivatives of Benzanthrone and Carbazole: Towards Damage-Resistive Information Recording and Security Probes. *Dyes and Pigments.* **2022**, *199*, 110082, doi:10.1016/j.dyepig.2022.110082.
21. Thomas, A.; Patil, P. S.; Siddlingeshwar, B.; Manohara, S. R.; Gummagol, N. B.; Krishna Chaitanya, G.; Kirilova, E. M. Nonlinear Optical Properties of Benzanthrone Derivatives with N’-Methylpiperazin-1-Yl and N’-Phenylpiperazin-1-Yl Substituents: Experimental and Quantum Chemical Study. *Opt. Laser Technol.* **2022**, *156*, 108616, doi:10.1016/j.optlastec.2022.108616.
22. Thomas, A.; Kirilova, E. M.; Nagesh, B. V.; Krishna Chaitanya, G.; Philip, R.; Manohara, S. R.; Sudeeksha, H. C.; Siddlingeshwar, B. Influence of Nitro Group on Solvatochromism, Nonlinear Optical Properties of 3-Morpholinobenzanthrone: Experimental and Theoretical Study. *J. Photochem. Photobiol. A. Chem.* **2023**, *437*, 114434, doi:10.1016/j.jphotochem.2022.114434.
23. Day, F. H. Nitration of the 13-Halogenobenzanthrones. *Journal of the Chemical Society (Resumed)* **1940**, 1474, doi:10.1039/jr9400001474.
24. Cerón-Carrasco, J. P.; Jacquemin, D.; Laurence, C.; Planchat, A.; Reichardt, C.; Sraïdi, K. Solvent Polarity Scales: Determination of New ET(30) Values for 84 Organic Solvents. *J. Phys. Org. Chem.* **2014**, *27*, 512–518, doi:10.1002/poc.3293.
25. Mucha, A.; Kafarski, P.; Berlicki, Ł. Remarkable Potential of the α-Aminophosphonate/Phosphinate Structural Motif in Medicinal Chemistry. *J. Med. Chem.* **2011**, *54*, 5955–5980, doi:10.1021/jm200587f.
26. Litim, B.; Djahoudi, A.; Meliani, S.; Boukhari, A. Synthesis and Potential Antimicrobial Activity of Novel α-Aminophosphonates Derivatives Bearing

Substituted Quinoline or Quinolone and Thiazole Moieties. *Medicinal Chemistry Research.* **2022**, *31*, 60–74, doi:10.1007/s00044-021-02815-5.

27. Rezaei, Z.; Khabnadideh, S.; Zomorodian, K.; Pakshir, K.; Nadali, S.; Mohtashami, N.; Faghih Mirzaei, E. Design, Synthesis, and Antifungal Activity of New α - Aminophosphonates. *Int. J. Med. Chem.* **2011**, *2011*, 1–11, doi:10.1155/2011/678101.
28. Varga, P. R.; Szabó, R. O.; Dormán, G.; Bősze, S.; Keglevich, G. Cytotoxic Activity of α-Aminophosphonic Derivatives Coming from the Tandem Kabachnik-Fields Reaction and Acylation. *Pharmaceuticals.* **2023**, *16*, 506, doi:10.3390/ph16040506.
29. Grzyś, E.; Bielecki, K.; Sarapuk, J. Aminophosphonate-Induced Changes of Betacyanine and Ionic Efflux. *Zeitschrift für Naturforschung C.* **2001**, *56*, 349–352, doi:10.1515/znc-2001-5-605.
30. Kafarski, P.; Lejczak, B. Biological Activity of Aminophosphonic Acids. *Phosphorus Sulfur Silicon Relat. Elem.* **1991**, *63*, 193–215, doi:10.1080/10426509108029443.
31. Reddy, N. B.; Sundar, C. S.; Krishna, B. S.; Santhisudha, S.; Sreelakshmi, P.; Nayak, S. K.; Reddy, C. S. Cellulose-SO3H Catalyzed Synthesis of Bis(α-Aminophosphonates) and Their Antioxidant Activity. *Organic Communications.* **2017**, *10*, 46–55, doi:10.25135/acg.oc.8.16.06.422.
32. Fouda, S. R.; El-Sayed, I. E.; Attia, N. F.; Abdeen, M. M.; Abdel Aleem, A. A. H.; Nassar, I. F.; Mira, H. I.; Gawad, E. A.; Kalam, A.; Al-Ghamdi, A. A.; et al. Mechanistic Study of Hg(II) Interaction with Three Different α-Aminophosphonate Adsorbents: Insights from Batch Experiments and Theoretical Calculations. *Chemosphere.* **2022**, *304*, 135253, doi:10.1016/j.chemosphere.2022.135253.
33. Imam, E. A.; Hashem, A. I.; Tolba, A. A.; Mahfouz, M. G.; El-Sayed, I. E.-T.; El-Tantawy, A. I.; Galhoum, A. A.; Guibal, E. Effect of Mono- vs. Bi-Functionality of Aminophosphonate Derivatives on the Enhancement of U(VI) Sorption: Physicochemical Properties and Sorption Performance. *J. Environ. Chem. Eng.* **2023**, *11*, 109951, doi:10.1016/j.jece.2023.109951.
34. Moumeni, O.; Mehri, M.; Kerkour, R.; Boublia, A.; Mihoub, F.; Rebai, K.; Khan, A. A.; Erto, A.; Darwish, A. S.; Lemaoui, T.; et al. Experimental and Detailed DFT/MD Simulation of α-Aminophosphonates as Promising Corrosion Inhibitor for XC48 Carbon Steel in HCl Environment. *J. Taiwan Inst. Chem. Eng.* **2023**, *147*, 104918, doi:10.1016/j.jtice.2023.104918.
35. Li, S.; Liu, R.; Han, X.; Ge, C.; Zhang, X. Diethyl α-Aminophosphonate Containing Lubricating Additives Synthesized from (3-Aminophenyl)Boronic Acid Pinacol Ester. *Inorg. Chem. Commun.* **2022**, *140*, 109477, doi:10.1016/j.inoche.2022.109477.
36. Górny vel Górniak, M.; Kafarski, P. Preparation of the Library of Fluorescent Aromatic Aminophosphonate Phenyl and Benzyl Esters. *Phosphorus Sulfur Silicon Relat. Elem.* **2016**, *191*, 511–519, doi:10.1080/10426507.2015.1094658.
37. Kuśnierz, A.; Chmielewska, E. Synthesis of Fluorescent Aminophosphonates by Green Chemistry Procedures. *Phosphorus Sulfur Silicon Relat. Elem.* **2017**, *192*, 700–705, doi:10.1080/10426507.2017.1308934.
38. Wang, Q.-M.; Gao, W.; Song, J.-L.; Liu, Y.; Qi, H.; Tang, X.-H. Synthesis, X-Ray Crystallographic Analysis and BSA Interaction of a New α-Aminophosphonate. *J. Appl. Spectrosc.* **2016**, *83*, 703–709, doi:10.1007/s10812-016-0351-9.
39. Lewkowski, J.; Rodriguez Moya, M.; Wrona-Piotrowicz, A.; Zakrzewski, J.; Kontek, R.; Gajek, G. Synthesis, Fluorescence Properties and the Promising

Cytotoxicity of Pyrene–Derived Aminophosphonates. *Beilstein Journal of Organic Chemistry.* **2016**, *12*, 1229–1235, doi:10.3762/bjoc.12.117.

40. Kraicheva, I.; Vodenicharova, E.; Tashev, E.; Tosheva, T.; Tsacheva, I.; Troev, K. Synthesis and NMR Characterization of Two Novel Anthracene-Derived BIS-Aminophosphonates. Basic Hydrolysis of Some Aminophosphonate Derivatives. *Phosphorus Sulfur Silicon Relat. Elem* **2012**, *187*, 660–667, doi:10.1080/10426507.2011.638349.
41. Varga, P. R.; Keglevich, G. Synthesis of α-Aminophosphonates and Related Derivatives; The Last Decade of the Kabachnik-Fields Reaction. *Molecules.* **2021**, *26*, 2511, doi:10.3390/molecules26092511.
42. Lüttringhaus, A.; Neresheimer, H. Zur Kenntnis Des Benzanthrons. *Justus Liebigs Ann. Chem.* **1929**, *473*, 259–289, doi:10.1002/jlac.19294730115.
43. Keglevich, G.; Bálint, E. The Kabachnik-Fields Reaction: Mechanism and Synthetic Use. *Molecules.* **2012**, *17*, 12821–12835, doi:10.3390/molecules171112821.
44. Kirilova, E. M.; Puckins, A. I.; Romanovska, E.; Fleisher, M.; Belyakov, S. V. Novel Amidine Derivatives of Benzanthrone: Effect of Bromine Atom on the Spectral Parameters. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2018**, *202*, 41–49, doi:10.1016/j.saa.2018.05.029.
45. Armignacco, O.; Caterini, L.; Marucci, G.; Ferri, F.; Bernardini, G.; Raponi, G. N.; Ludovisi, A.; Bossù, T.; Morales, M. A. G.; Pozio, E. Human Illnesses Caused by Opisthorchis Felineus Flukes, Italy. *Emerg. Infect. Dis.* **2008**, *14*, 1902–1905, doi:10.3201/eid1412.080782.
46. Kaur, N.; Gauri Anthraquinone Appended Chemosensors for Fluorescence Monitoring of Anions and/or Metal Ions. *Inorganica Chim. Acta.* **2022**, *536*, 120917, doi:10.1016/j.ica.2022.120917.
47. Bin Huang; Ji, Y.; Li, Z.; Zhou, N.; Jiang, W.; Feng, Y.; Lin, B.; Sun, Y. Simple Aggregation-Induced Delayed Fluorescence Materials Based on Anthraquinone Derivatives for Highly Efficient Solution-Processed Red OLEDs. *J. Lumin.* **2017**, *187*, 414–420, doi:10.1016/j.jlumin.2017.03.038.
48. Yang, L.; Fu, Z.; Niu, X.; Zhang, G.; Cui, F.; Zhou, C. Probing the Interaction of Anthraquinone with DNA by Spectroscopy, Molecular Modeling and Cancer Cell Imaging Technique. *Chem. Biol. Interact.* **2015**, *233*, 65–70, doi:10.1016/j.cbi.2015.03.026.
49. Malik, M. S.; Alsantali, R. I.; Jassas, R. S.; Alsimaree, A. A.; Syed, R.; Alsharif, M. A.; Kalpana, K.; Morad, M.; Althagafi, I. I.; Ahmed, S. A. Journey of Anthraquinones as Anticancer Agents – a Systematic Review of Recent Literature. *RSC Adv.* **2021**, *11*, 35806–35827, doi:10.1039/D1RA05686G.
50. Zhao, L.; Zheng, L. A Review on Bioactive Anthraquinone and Derivatives as the Regulators for ROS. *Molecules.* **2023**, *28*, 8139, doi:10.3390/molecules28248139.
51. Bespalaya, Y. V.; Kondakov, A. V.; Travina, O. V.; Khrebtova, I. S.; Kropotin, A. V.; Aksenova, O. V.; Gofarov, M. Yu.; Lyubas, A. A.; Tomilova, A. A.; Vikhrev, I. V. First Record of Metacercariae Trematodes Opisthioglyphe Ranae (Digenea: Telorchiidae) and Echinostoma Bolschewense (Digenea: Echinostomatidae) in Dreissena Polymorpha (Bivalvia: Dreissenidae) from the Don and Volga River Basins, Russia. *Ecol Montenegrina.* **2022**, *54*, 57–76, doi:10.37828/em.2022.54.8.
52. Monçalves, M.; Zanotto, G. M.; Toldo, J. M.; Rampon, D. S.; Schneider, P. H.; Gonçalves, P. F. B.; Rodembusch, F. S.; Silveira, C. C. Dipolar Vinyl Sulfur

Fluorescent Dyes. Synthesis and Photophysics of Sulfide, Sulfoxide and Sulfone Based D–π–A Compounds. *RSC Adv.* **2017**, *7*, 8832–8842, doi:10.1039/C6RA27989A.

53. Rachi, Y.; Yamakado, R.; Okada, S. Synthesis of Dyes with a Sulfur-Containing Heterocyclic Donor and a Pyrroline-Type Acceptor. *Dyes and Pigments.* **2018**, *159*, 345–351, doi:10.1016/j.dyepig.2018.06.032.
54. Sims, M. T.; Abbott, L. C.; Cowling, S. J.; Goodby, J. W.; Moore, J. N. Molecular Design Parameters of Anthraquinone Dyes for Guest-Host Liquid-Crystal Applications: Experimental and Computational Studies of Spectroscopy, Structure, and Stability. *The Journal of Physical Chemistry C.* **2016**, *120*, 11151–11162, doi:10.1021/acs.jpcc.6b03607.
55. Cowling, S. J.; Ellis, C.; Goodby, J. W. Anthraquinone Liquid Crystal Dichroic Dyes – a New Form of Chromonic Dye? *Liq. Cryst.* **2011**, *38*, 1683–1698, doi:10.1080/02678292.2011.620181.
56. Ye, J.; Gao, Y.; He, L.; Tan, T.; Chen, W.; Liu, Y.; Wang, Y.; Ning, G. Efficient Blue-Emitting Molecules by Incorporating Sulfur-Containing Moieties into Triarylcyclopentadiene: Synthesis, Crystal Structures and Photophysical Properties. *Dyes and Pigments.* **2016**, *124*, 145–155, doi:10.1016/j.dyepig.2015.09.018.
57. Liu, Y.; Yu, Y.; Zhao, Q.; Tang, C.; Zhang, H.; Qin, Y.; Feng, X.; Zhang, J. Fluorescent Probes Based on Nucleophilic Aromatic Substitution Reactions for Reactive Sulfur and Selenium Species: Recent Progress, Applications, and Design Strategies. *Coord. Chem. Rev.* **2021**, *427*, 213601, doi:10.1016/j.ccr.2020.213601.
58. Vaidyanathan, T.; Seshadri, S. Nucleophilic Substitution Reactions on 3-Bromo- and 3-Nitrobenzanthrones. *Dyes and Pigments.* **1984**, *5*, 431–436, doi:10.1016/0143-7208(84)80035-2.
59. Melville, O. A.; Grant, T. M.; Rice, N. A.; Wang, B.; Josse, P.; Lessard, B. H. Functionalization of Commercial Pigment Hostasol Red GG for Incorporation into Organic Thin-Film Transistors. *New Journal of Chemistry.* **2020**, *44*, 845–851, doi:10.1039/C9NJ04851K.
60. Montanari, S.; Paradisi, C.; Scorrano, G. Thiol Anions in Nucleophilic Aromatic Substitution Reactions with Activated Aryl Halides. Attack on Carbon vs Attack on Halogen. *J. Org. Chem.* **1993**, *58*, 5628–5631, doi:10.1021/jo00073a020.
61. Campodónico, P. R.; Alarcón-Espósito, J.; Olivares, B. Kinetics and Reaction Mechanism of Biothiols Involved in SNAr Reactions: An Experimental Study. *Front. Chem.* **2022**, *10*, doi:10.3389/fchem.2022.854918.
62. Rohrbach, S.; Smith, A. J.; Pang, J. H.; Poole, D. L.; Tuttle, T.; Chiba, S.; Murphy, J. A. Concerted Nucleophilic Aromatic Substitution Reactions. *Angewandte Chemie International Edition.* **2019**, *58*, 16368–16388, doi:10.1002/anie.201902216.
63. Kunda, G.; Akhmadullin, R. M.; Zakirov, R. K.; Akhmadullina, F. Y.; Gizyatullov, R. N.; Madaminov, N. V.; Musin, L. I. Thiol Synthesis Methods: A Review. *Journal of Sulfur Chemistry.* **2024**, 1–34, doi:10.1080/17415993.2024.2428607.
64. Hansch, C.; Leo, A.; Taft, R. W. A Survey of Hammett Substituent Constants and Resonance and Field Parameters. *Chem. Rev.* **1991**, *91*, 165–195, doi:10.1021/cr00002a004.
65. Maeda, H.; Maeda, T.; Mizuno, K.; Fujimoto, K.; Shimizu, H.; Inouye, M. Alkynylpyrenes as Improved Pyrene-Based Biomolecular Probes with the Advantages

of High Fluorescence Quantum Yields and Long Absorption/Emission Wavelengths. *Chemistry – A European Journal.* **2006**, *12*, 824–831, doi:10.1002/chem.200500638.

66. Chen, M.; Wei, J.; Zhang, Y.; Wu, L.; Tan, L.; Shi, S.; Shi, J.; Ji, L. 2,7-Carbazole Derived Organoboron Compounds: Synthesis and Molecular Fluorescence. *Front. Chem.* **2021**, *9*, doi:10.3389/fchem.2021.754298.
67. Yang, J.; Dass, A.; Rawashdeh, A.-M. M.; Sotiriou-Leventis, C.; Panzner, M. J.; Tyson, D. S.; Kinder, J. D.; Leventis, N. Arylethynyl Substituted 9,10-Anthraquinones: Tunable Stokes Shifts by Substitution and Solvent Polarity. *Chemistry of Materials.* **2004**, *16*, 3457–3468, doi:10.1021/cm049590g.
68. Yang, J.-X.; Wang, X.-L.; Wang, X.-M.; Xu, L.-H. The Synthesis and Spectral Properties of Novel 4-Phenylacetylene-1,8-Naphthalimide Derivatives. *Dyes and Pigments.* **2005**, *66*, 83–87, doi:10.1016/j.dyepig.2004.07.015.
69. Bai, J.-Y.; Xie, Y.-Z.; Wang, C.-J.; Fang, S.-Q.; Cao, L.-N.; Wang, L.-L.; Jin, J.-Y. A Quninolylthiazole Derivatives as an ICT-Based Fluorescent Probe of Hg(II) and Its Application in Ratiometric Imaging in Live HeLa Cells. *J. Fluoresc.* **2018**, *28*, 795–800, doi:10.1007/s10895-018-2241-4.
70. Altınok, E.; Smith, Z. C.; Thomas, S. W. Two-Dimensional, Acene-Containing Conjugated Polymers That Show Ratiometric Fluorescent Response to Singlet Oxygen. *Macromolecules.* **2015**, *48*, 6825–6831, doi:10.1021/acs.macromol.5b01076.
71. Tlach, B. C.; Tomlinson, A. L.; Bhuwalka, A.; Jeffries-EL, M. Tuning the Optical and Electronic Properties of 4,8-Disubstituted Benzobisoxazoles via Alkyne Substitution. *J. Org. Chem.* **2011**, *76*, 8670–8681, doi:10.1021/jo201078w.
72. Saeed, M. A.; Le, H. T. M.; Miljanić, O. Š. Benzobisoxazole Cruciforms as Fluorescent Sensors. *Acc. Chem. Res.* **2014**, *47*, 2074–2083, doi:10.1021/ar500099z.
73. Yamaguchi, Y.; Matsubara, Y.; Ochi, T.; Wakamiya, T.; Yoshida, Z. How the π Conjugation Length Affects the Fluorescence Emission Efficiency. *J. Am. Chem. Soc.* **2008**, *130*, 13867–13869, doi:10.1021/ja8040493.
74. Maļeckis, A.; Avotiņa, L.; Ķizāne, G.; Pučkins, A.; Osipovs, S.; Kirilova, E. New Fluorescent Heterocyclic Compounds Derived From 3-Cyanobenzanthrone. *Polycycl. Aromat. Compd.* **2022**, *42*, 5508–5520, doi:10.1080/10406638.2021.1939068.
75. Sonogashira, K.; Tohda, Y.; Hagihara, N. A Convenient Synthesis of Acetylenes: Catalytic Substitutions of Acetylenic Hydrogen with Bromoalkenes, Iodoarenes and Bromopyridines. *Tetrahedron Lett.* **1975**, *16*, 4467–4470, doi:10.1016/S0040-4039(00)91094-3.
76. Kanwal, I.; Mujahid, A.; Rasool, N.; Rizwan, K.; Malik, A.; Ahmad, G.; Shah, S. A. A.; Rashid, U.; Nasir, N. M. Palladium and Copper-Catalyzed Sonogashira Cross-Coupling an Excellent Methodology for C-C Bond Formation over 17 Years: A Review. *Catalyst.s* **2020**, *10*, 443, doi:10.3390/catal10040443.
77. Hartwig, J. F. Electronic Effects on Reductive Elimination To Form Carbon−Carbon and Carbon−Heteroatom Bonds from Palladium(II) Complexes. *Inorg. Chem.* **2007**, *46*, 1936–1947, doi:10.1021/ic061926w.

Armands Maļeckis was born in 1997 in Daugavpils. He obtained an academic Bachelor's degree in Engineering Sciences in Chemical Technology from Riga Technical University (2019) and a Master's degree in Natural Sciences in Chemistry from Daugavpils University (2021). He is a co-author of ten original publications, serving as the corresponding author for eight of them. Currently, he is an organic chemist at Enamine Ltd and continues his research in the chemistry of fluorescent compounds at Daugavpils University as a researcher.