ABSTRACT

of the dissertation by Ablaykhan Nurbayevich Iskanderov on the topic "New π-conjugated oligomers based on azulene structures: synthesis and photophysical properties", submitted for the degree of Doctor of Philosophy (PhD) in the specialty 6D060600 – Chemistry

Dissertation research topic: "New π-conjugated oligomers based on azulene structures: synthesis and photophysical properties".

The dissertation is devoted to the investigation of the Suzuki–Miyaura cross-coupling reaction and the development of synthetic methods for new π-conjugated azulene co-oligomers containing electron-donating diphenylamine and carbazolyl groups at the key 2- and 6-positions of the azulene core. The research also focuses on studying their electronic absorption and fluorescence emission properties in the visible region of the electromagnetic spectrum.

Objective of the dissertation research: The objective of this dissertation research is to synthesize a representative series of new π-conjugated azulene co-oligomers containing electron-donating diphenylamine and carbazolyl groups at the 2- and 6-positions of the azulene core, and to investigate their electronic absorption and fluorescence emission properties in the visible region of the spectrum.

Research objectives:

• To investigate the selective borylation of azulene and the Suzuki–Miyaura cross-coupling reaction of borylated azulenes with diphenylamine;

• To investigate the selective halogenation of azulene and the cross-coupling reaction of haloazulenes with carbazole**;**

• To study the electronic absorption and fluorescence emission properties of the synthesized diphenylamine-substituted azulenes**,** as well as diphenylamine- and carbazole-containing azulene co-oligomers**,** in the UV–Vis spectral region**;**

• To investigate the relationship between the molecular structure and the photophysical properties of the synthesized compounds using Density Functional Theory (DFT) calculations**;**

• To investigate the redox properties of the synthesized compounds using cyclic voltammetry (CV)**.**

Research Methods: The study employed modern methods of organic and organoelement synthesis, including Suzuki–Miyaura cross-coupling reactions**,** cascade transformations, condensation reactions, aromatic substitution reactions, and others. Modern physicochemical characterization techniques were also used, including ^{1}H NMR**,** ^{13}C NMR**,** IR spectroscopy**,** mass spectrometry**,** UV–Vis spectrophotometry**,** spectrofluorimetry**,** thermogravimetric analysis (TGA)**,**

differential scanning calorimetry (DSC)**,** chromatographic methods (flash column chromatography and thin-layer chromatography, TLC), elemental analysis**,** and Density Functional Theory (DFT) calculations**.**

Main provisions submitted for defense.

1. New conjugated azulene compounds containing diphenylamine fragments at the 2- and 6-positions were successfully synthesized. The Suzuki–Miyaura cross-coupling reaction played a key role in their preparation. Investigation of their photophysical properties revealed new and intense absorption and emission bands in the visible region of the spectrum. Furthermore, it was established that the appearance of unique fluorescence emissions in the blue and green photoluminescence regions, which are absent in the parent azulene molecule, is caused by the strong electron-donating effect of the diphenylamine groups. These substituents significantly modify the electronic structure of azulene, enabling an allowed $\pi \rightarrow \pi^*$ electronic transition.

2. New 2,6-diphenylamine-substituted azulene conjugated co-oligomers with both linear and branched architectures were successfully synthesized. The synthesis of these molecules was achieved through the Suzuki–Miyaura cross-coupling reaction. Their optical properties revealed the appearance of new, intense, and broad absorption and emission bands in the visible spectral region. Moreover, strong fluorescence emission in the green and orange regions of the spectrum was found to arise from the positive resonance effect characteristic of the diphenylamine fragments. The influence of these electron-donating groups on the acceptor azulene moieties significantly alters their electronic structure, particularly the energy levels and energy gaps between the frontier molecular orbitals HOMO and LUMO.

3. New azulenic conjugated co-oligomers containing carbazolyl substituents at positions 1, 2, 3, and 6 have been synthesized. The cross-coupling reaction played an important role in this synthesis. Photophysical properties revealed new and intense absorption and emission bands in the visible region. In addition, it was found that the strong fluorescent emission in the blue spectral range is attributed to the pronounced electron-donating properties of the carbazolyl substituents. This effect is a key factor enabling the HOMO → LUMO electronic transition in azulene.

Main results of the study:

1. Based on Suzuki–Miyaura cross-coupling reactions and iridium-complex-catalyzed direct borylation, new methods for the synthesis of π-conjugated diphenylamine- and carbazolyl-substituted azulenic compounds with linear and branched structures were developed for the first time. These methods are characterized by high selectivity and high yields.

2. For the first time, new π-conjugated diphenylamine-substituted azulenes**,** namely 2-(N,N-diphenylamino)azulene and 2,6-bis(N,N-diphenylamino)azulene**,**

were synthesized. Investigation of their photophysical properties demonstrated intense absorption (ε = 24,637 and 86,888 M^{-1} cm^{-1}) and visible-light emission (I = 257 and 264 a.u.) in the wavelength range of 400–600 nm**.** It was established that the visible fluorescence emissions with λ_{em} values of 495 and 525 nm**,** which are absent in the parent azulene, result from the electron-donating effect of the diphenylamine groups at the C-2 and C-6 positions**.** This electronic influence significantly modifies the electronic structure of azulene and promotes an allowed π→π* electronic transition.

3. For the first time, new π-conjugated diphenylamine–azulene co-oligomers with linear and branched architectures were synthesized, namely 6,6-bis(N,N-diphenylamino)-2,2′-(4-(diphenylamino)phenyl)bisazulene and 6,6,6-tris(N,N-diphenylamino)-2,2′,2″-(4-(triphenylamino)phenyl)trisazulene. Investigation of their photophysical properties demonstrated intense absorption (ε = 22,447 and 24,621 M^{-1} cm^{-1}) and visible-light emission in the 410–700 nm spectral range. In particular, these compounds exhibited strong fluorescence emission in the green and orange regions with emission maxima at 510 and 590 nm, respectively, and photoluminescence quantum yields **(**PLQY**)** of 56% and 65%**.** It was shown that these remarkable optical properties arise from the positive resonance effect of the aniline fragments, which significantly modify the electronic structure of the parent azulene framework. In particular, these substituents alter the energy levels and energy gaps between the frontier molecular orbitals HOMO and LUMO, leading to enhanced photophysical performance.

4. For the first time, new π-conjugated carbazolyl–azulene co-oligomers, namely 1,2,3-tris(carbazolyl)azulene and 1,2,3,6-tetrakis(carbazolyl)azulene, were synthesized. Investigation of their photophysical properties revealed that these compounds possess significant absorption (ε = 21,132 and 36,666 M^{-1} cm^{-1}) and emission capabilities in the visible spectral range of 380–600 nm**.** It was demonstrated that azulene derivatives bearing carbazolyl substituents at the 1, 2, 3, and 6 positions exhibit intense blue photoluminescence, with emission maxima **(**λPL**)** at 444 and 490 nm and photoluminescence quantum yields (ΦPL) of 0.12 and 0.25, respectively. Such emission behavior is not observed in the parent azulene molecule. This phenomenon is attributed **to** intramolecular donor–acceptor interactions, which facilitate an allowed HOMO→LUMO electronic transition and significantly enhance the photophysical properties of the synthesized compounds.

5. The synthesized conjugated azulene co-oligomers containing diphenylamine and carbazolyl fragments exhibit significant potential for applications in organic optoelectronics. Their unique electronic and photophysical properties make them promising candidates for use in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic photovoltaic cells (OPVs). The

implementation of these materials may contribute to improved energy efficiency, enhanced device stability, and the development of environmentally friendly energy technologies. Furthermore, these compounds represent a new class of functional organic materials with considerable potential for next-generation optoelectronic applications.

Novelty and significance of the obtained results. As a result of this dissertation research, new π-conjugated 2- and 2,6-diphenylamine-substituted azulenes were synthesized for the first time in high yields using the Suzuki–Miyaura cross-coupling reaction. It was established that these compounds exhibit intense absorption and emission of visible light in the wavelength range of 400–600 nm. Their unique optical properties, particularly fluorescence emission in the blue and green photoluminescence regions (λ_{em} = 495 and 525 nm), which are absent in the parent azulene molecule, were shown to originate from the strong electron-donating effect of the diphenylamine groups. These substituents significantly alter the electronic structure of azulene and promote an allowed π→π* electronic transition. Furthermore, new π-conjugated 2,6-diphenylamine–azulene co-oligomers with linear and branched architectures were synthesized in high yields under Suzuki–Miyaura cross-coupling conditions. The obtained co-oligomers demonstrated strong absorption and emission in the visible spectral region of 410–700 nm, exhibiting intense fluorescence in the green and orange regions with emission maxima at 510 and 590 nm, respectively. These optical properties were found to arise from the positive resonance effect of the aniline fragments, which substantially modify the electronic structure of the azulene core, particularly the energy levels and energy gaps between the frontier molecular orbitals HOMO and LUMO. In addition, new carbazolyl-substituted conjugated azulene co-oligomers, including 1,2,3-tris(carbazolyl)azulene and 1,2,3,6-tetrakis(carbazolyl)azulene, were synthesized in high yields via cross-coupling reactions. These compounds exhibited significant absorption and emission capabilities in the long-wavelength visible region, spanning 400–600 nm. Moreover, azulene derivatives bearing carbazolyl substituents at the 1, 2, 3, and 6 positions displayed unique photophysical properties characterized by intense blue photoluminescence (λPL = 444 and 490 nm), which is not observed in the parent azulene. This behavior was attributed to the electron-donating nature of the carbazolyl groups, which strongly influence the electronic structure of azulene and create favorable conditions for an allowed HOMO→LUMO electronic transition.

The significance of this work lies in the development of new synthetic methods for the preparation of a wide range of novel π-conjugated azulene-containing co-oligomers possessing valuable photophysical properties, including intense electronic absorption and fluorescence emission in the visible region of the spectrum.

The dissertation research demonstrated the potential application of several of the synthesized azulene co-oligomers in various organic electronic devices. The synthetic methodologies developed in this work, which are protected by patents of the Republic of Kazakhstan, enable the design and preparation of new functional organic materials with tailored optoelectronic properties.

Compliance with scientific development priorities and national programs. The dissertation research was carried out within the framework of the Targeted Funding Program of the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan entitled "Development of New TADF Organic Luminophores Based on π-Conjugated Azulene Co-oligomers for Third-Generation Organic Light-Emitting Diodes (OLEDs)" (Grant No. BR21882309) for the period 2023–2025. The research was conducted under the national priority area "Intellectual Potential of the Country" and within the scientific field of "Natural Sciences."

Author's contribution. The author was directly involved in all stages of the dissertation research, including the preparation of each publication, from formulating the research objectives and planning the experiments to discussing and presenting the results. The synthetic part of the work was carried out personally by the author. In addition, the author investigated the photophysical properties (electronic absorption and fluorescence), redox properties, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and spectrometric characteristics of the synthesized compounds. The author also participated in the interpretation and analysis of the experimental data obtained throughout the study.

The main results of the research are reflected in 7 published articles and 3 patents of the Republic of Kazakhstan, including 3 articles published in scientific journals ranked in the first and/or second quartile according to the impact factor data of Clarivate Analytics:

1. Nurlan Merkhatuly, Ablaykhan Iskanderov, Saltanat Abeuova, Amantay Iskanderov and Saltanat Zhokizhanova. Introduction of Electron Donor Groups into the Azulene Structure: The Appearance of Intense Absorption and Emission in the Visible Region // Molecules. – 2024. – Vol. 29, Issue 14. – Article No. 3354 (the doctoral student is the corresponding author). The journal impact factor for 2023 is 4.2, with a Q2 quartile ranking in multidisciplinary chemistry. The journal has a 2023 CiteScore of 7.4 and an 83rd percentile in Chemistry (miscellaneous). Author's contribution: software, validation, formal analysis, investigation, data curation, visualization.

2. Nurlan Merkhatuly, Amantay Iskanderov, Saltanat Abeuova, Ablaykhan Iskanderov and Saltanat Zhokizhanova. Conjugated Diphenylaniline–Azulene Co-Oligomers with Intense Absorption and Emission in the Visible Region // Molecules. – 2024. – Vol. 29, Issue 21. – Article No. 5041. The journal impact factor for 2023 is 4.2, with a Q2 quartile ranking in multidisciplinary chemistry. The journal has a

2023 CiteScore of 7.4 and an 83rd percentile in Chemistry (miscellaneous). Author's contribution: software, validation, formal analysis, investigation, data curation, visualization.

3. Amantay Iskanderov, Nurlan Merkhatuly, Ablaykhan Iskanderov, Saltanat Abeuova and Pavel Vojtisek. Synthesis of Conjugated Tris- and Tetrakis (Carbazolyl)Azulenes with Intense Emission in the Visible Range // Molecules. – 2025. – Vol. 30, Issue 13. – Article No. 2797. The journal impact factor for 2024 is 4.6, with a Q2 quartile ranking in multidisciplinary chemistry. The journal has a 2024 CiteScore of 8.6 and an 87th percentile in Organic Chemistry. Author's contribution: software, validation, formal analysis, investigation, data curation, visualization.

4. N. Merkhatuly, A.N. Iskanderov, S.B. Abeuova, A.N. Iskanderov, A.O. Bulumbaeva. Синтез и фотофизические свойства сопряженных N,N – дифениланилиназуленов (Synthesis and Photophysical Properties of Conjugated N,N-DiphenylanilineAzulenes) News of the National Academy of Sciences of the Republic of Kazakhstan. Series Chemistry and Technology. – No. 463(2). – 2025. – Pp. 157–169. Author's contribution: software, validation, investigation, data curation, visualization.

5. N. Merkhatuly, A.N. Iskanderov, S.B. Abeuova, G.M. Kadirberlina, A.S. Seitkan, A.M. Kemelbekova. Синтез, электронная и эмиссионная спектроскопия дифениланилин-азуленовых со-олигомеров (Synthesis, Electronic and Emission Spectroscopy of Diphenylaniline–Azulene Co-Oligomers) // Chemical Bulletin of Kazakh National University. – No. 114. – 2025. – Pp. 44–49. Author's contribution: software, validation, investigation, data curation, visualization.

6. N. Merkhatuly, A.N. Iskanderov, S.K. Zhokizhanova, Kh.B. Omarov, A.N. Iskanderov, P. Vojtisek. Азоттан тұратын қосарланған азулен қосылыстарының фотофизикалық қасиеттері (Photophysical Properties of Nitrogen-Containing Conjugated Azulene Compounds) // Vestnik KazUTB. – No. 28(3). – 2025. – Pp. 244–253. Author's contribution: software, validation, investigation, data curation.

7. N. Merkhatuly, A.N. Iskanderov, S.K. Zhokizhanova, Kh.B. Omarov, A.N. Iskanderov, A.O. Bulumbaeva. Көрінетін спектрде белсенді сіңіру және шығаруы бар донорлы алмастырған азулен қосылыстары (Donor-Substituted Azulene Compounds with Active Absorption and Emission in the Visible Spectrum) // Vestnik KazUTB. – No. 29(4). – 2025. – Pp. 245–254. Author's contribution: software, validation, investigation, data curation.

8. A.N. Iskanderov, R.N. Zhorabekov, M.A. Nurtayeva, N. Merkhatuly. Синтез новых арилазуленов с использованием кросс-сочетания Кумады (Synthesis of New Arylazulenes Using Kumada Cross-Coupling) // Proceedings of the X Beremzhanov Congress on Chemistry and Chemical Technology. – Almaty, 2019. – P. 133. Author's contribution: software, validation, investigation, data curation.

9. A.N. Iskanderov, A.N. Karimova, A.M. Kassymova, N. Merkhatuly. Синтез донорно-акцепторных производных азулена (Synthesis of Donor–Acceptor Azulene Derivatives) // Global Science and Innovation 2021: Central Asia: XII International Scientific and Practical Conference. – Nur-Sultan, 2021. – Pp. 80–81. Author's contribution: software, validation, investigation, data curation.

10. N. Merkhatuly, A.N. Iskanderov, A.A. Dzhadenova, Zh.E. Shauen, M.M. Ibrayeva. Синтез новых 1,3-дизамещенных азуленов (Synthesis of New 1,3-Disubstituted Azulenes) // XIII Toraighyrov Readings International Scientific and Practical Conference. – Pavlodar, 2021. – Pp. 164–165. Author's contribution: software, validation, investigation, data curation.

11. N. Merkhatuly, A.N. Iskanderov, S.K. Zhokizhanova, A.N. Iskanderov. Способ получения донорно-акцепторного сопряженного 2,6-бис(N,N-дифениланилин)азулена (Method for Obtaining Donor–Acceptor Conjugated 2,6-bis(N,N-diphenylaniline)azulene) // Certificate of State Registration of Rights to an Object of Copyright No. 10636, dated 30.05.2025. Author's contribution: software, validation, investigation, data curation.

12. N. Merkhatuly, A.N. Iskanderov, S.B. Abeuova, A.N. Iskanderov. Способ получения push-pull 2-(N,N-дифениланилин)азулена (Method for Obtaining Push–Pull 2-(N,N-diphenylaniline)azulene) // Certificate of State Registration of Rights to an Object of Copyright No. 10855, dated 11.07.2025. Author's contribution: software, validation, investigation, data curation.

13. N. Merkhatuly, A.N. Iskanderov, S.K. Zhokizhanova, A.N. Iskanderov. Способ получения донорно-акцепторного сопряженного 2,6-бис(9H-карбозолил)азулена (Method for Obtaining Donor–Acceptor Conjugated 2,6-bis(9H-carbazolyl)azulene) // Certificate of State Registration of Rights to an Object of Copyright No. 11362, dated 07.11.2025. Author's contribution: software, validation, investigation, data curation.