

## Review

of the materials, submitted for participation in a competition for the academic position "Associate Professor" in a Professional field 4.2. "Chemical Sciences" (Theoretical Chemistry), published in the State Gazette, issue 63 of 30.07.2021 for the needs of the Faculty of Chemistry and Pharmacy at Sofia University "St. Kliment Ohridski"

The only candidate for the academic position "Associate Professor" in the competition announced in the State Gazette no. 63 from 30.07.2021, is *Chief Assistant Professor Dr. Julia Ruslanova Romanova* (<https://orcid.org/0000-0001-6668-0879>, Author ID (Scopus): 36832298900).

Julia Romanova was born on March 19, 1983. She graduated from the Faculty of Chemistry at Sofia University in 2006 with professional qualification "Master of Computational Chemistry". In 2010, after successful performance of a PhD thesis on "Influence of the environment on the geometry, electronic structure and magnetic properties of polyaniline", under the scientific supervision of Prof. Alia Tadjer (from the Bulgarian side), Julia Romanova obtained the educational and scientific degree "Doctor". During her education and scientific career, she carried out a number of fruitful specializations in foreign universities and scientific institutes (Belgium, Great Britain, Germany).

### *General characteristics of the received materials*

The presented by Dr. Romanova materials for participation in the present competition are in full compliance with the requirements of the Law for development of the academic staff in Republic of Bulgaria and the Regulations for its implementation, the Regulations on the terms and conditions for obtaining scientific degrees and occupation academic positions at Sofia University and the Recommended Criteria of the Faculty of Chemistry and Pharmacy for Professional field 4.2. "Chemical Sciences".

The reference of Dr. Romanova for the implementation of the minimal national requirements under Art. 2b of the Law for development of the academic staff in Republic of Bulgaria for the academic position "Associate Professor" shows that the candidate meets the required minimum for all groups of indicators.

### *Scientific publications*

*The total number of scientific papers* of Dr. Julia Romanova is 31. Of these, 24 scientific publications have found a place on the pages of journals with IF and SJR, 4 are book chapters, 2 are articles in conference proceedings without IF and SJR, and 1 patent. The distribution of the scientific publications by quartile of the journals is as follows: 15 are published in journals of category Q1, 4 - in journals of category Q2, 4 - in journals of category Q3 and 1 is in a journal of category Q4. In 10 of the scientific papers the candidate is the first author, and in 8 of them she is the corresponding author. The scientific papers were published in a relatively short period of time (2009-2021), which testifies to the active research of the candidate after graduation. Dr. Romanova's investigations has been accompanied by numerous participations in research projects

(25) and scientific forums in the country and abroad (24). According to the SCOPUS database, at the time of preparation of the documents for participation in this competition, the total number of citations in the period 2007-2021 is 249 (excluding the auto-citations of all authors), the h-index is 11.

*The number of the selected scientific papers for participation in the competition* for the academic position "Associate Professor" is 15. All they are published after acquisition of the "Doctor" degree in the period 2010-2021. Of these, 14 are scientific publications in journals with IF and SJR, and 1 is a book chapter. 9 of the publications were published in journals of category Q1, 4 - in journals of category Q2 and 1 - in a journal of category Q4. In 6 of the publications the candidate is the first author, and in 5 - the corresponding author. The selected for the competition publications describe valuable in depth investigations on topics of the present day, contain a lot of new data and contributions in the field of computational material science and with them Dr. Romanova meets the required minimum for the academic position "Associate Professor" as to groups of indicators B (т. 4) and Г (т. 7 и 8).

#### *Habilitation Work*

In fulfillment of the Recommended Criteria for academic position "Associate Professor" at Faculty of Chemistry and Pharmacy, Sofia University, Dr. Romanova presented a Habilitation Work, for which she has chosen an intriguing and promising title: "Handbook for hunting and design of chromophores for singlet fission". In it, based on a literature review and own research, the first steps and future perspectives for the development of a relatively new scientific topic, defined as search, discovery and modeling of new chromophores for singlet fission, are presented.

For the research on the topic "singlet fission", Dr. Romanova has selected a series of 14 potential chromophores for singlet fission based on diboron-doped anthracenes and phenanthrenes. Molecular modeling has been performed with a set of appropriate computational methods and approximations at different levels of theory. The computational procedure is complex and started with structure optimizations (MP2/aug-cc-pVDZ) and calculations of the diradical character (PUHF/6-31G\*\*). To reveal the relationship between the topology, electronic structure (open-shell character) and singlet fission propensity, electronic structure calculations at the multiconfigurational wave function level of theory have been performed on top of the MP2-optimized ground-state geometries (RASPT2/aug-cc-pVDZ). The use of the multireference second-order approach is important for the accurate description of open-shell molecules since it allows to take into account both static and dynamic electron correlation effects. As a result, the calculated excitation energies (SA RASPT2) and the diradical character (SS RASPT2) were accurately evaluated and reliably used further for interpretation of the absorption properties of the studied molecules and estimation of their singlet fission proclivity. The analysis of the results, obtained from the state-of-the-art multiconfigurational calculations and interpreted in terms of Hückel, Clar и Kekulé theories, has allowed to reveal the fundamental interplay between the molecular topology, the nature of the electron density distribution (open-shell character) and the proclivity to singlet fission of the compounds. The results have shown that the boron-doping of polycyclic aromatic hydrocarbons and the variation of molecular topology are successful strategies for the in silico design of new singlet fission chromophores. Based on their photophysical

properties, several boron-doped compounds have been proposed as potential singlet fission materials with application in organic solar cells.

To assess the laboratory stability of quinone methides, a methodology has been proposed by calculations of their geometry (B3LYP/6-31G\*), diradical character (PUHF/6-31G\*\*), global and local reactivity indices, chemometric analysis and Clar's theory. As a result, classification model for laboratory stability of quinone methides has been developed based on the calculated quantum chemical descriptors. The studies convincingly prove that reactivity indices are reliable and can be used in the design of laboratory-stable photovoltaic materials, as well as to be successfully implemented in chemometric approaches for the discovery of new chromophores for singlet fission.

The diradical character was used as the main descriptor in creating a machine-learning based algorithm that quickly predicts whether a molecule is a potential chromophore for singlet fission ( $DRC \neq 0$ ) or it is a classic chromophore with a closed electronic shell. The calculation procedure included semiempirical (PM6) geometry optimization and prove of all the structures, evaluation of quantum chemical descriptors (HOMO and LUMO energies, dipole moment ( $\mu$ ), static polarizability ( $\alpha$ ), first ( $\beta$ ) and second ( $\gamma$ ) hyperpolarizability), as well as CASSCF(2,2)/CIS+INDO/S calculations of the vertical excitation energies at PM6 geometries with a minimum active space (HOMO, LUMO and two electrons). The proposed procedure provided automation without wrong choice of orbitals ( $\sigma$ -type), speed, reliability and estimation of the weight of the double-excited configuration in ground state ( $W^{ab}$ ), which is the other definition/measure of the diradical character. Quantum chemical descriptors were derived ( $E(S_1)$ ,  $E(S_2)$ ,  $E(T_1)$ ,  $E(T_2)$ ,  $f(S_1)$  and  $W^{ab}$ ), from which the two conditions for singlet fission,  $\Delta E_{ST}$  and  $\Delta E_{TT}$  (included in the descriptor set) were evaluated.

As a result of the research, a working database was created, containing 1545 molecules, of which 1/3 are of diradical character and 2/3 are of zero character. An artificial neural network has been trained, which qualitatively classifies molecules by diradical character (zero or non-zero). The neural network reaches 88% accuracy, which proves the reliability of the developed model for detecting molecules with non-zero diradical character and ability to singlet fission. It has been shown that combining DRC calculations and reactivity indices with chemometric methods is an extremely valuable approach in interpreting the laboratory stability of partially open electron shell organic molecules. The model for detection of molecules-potential chromophores for singlet fission, which are characterized by laboratory stability, is to be improved.

Dr. Romanova's research related to the search, discovery and modeling of new chromophores for singlet fission is characterized by an innovative research approach, including quantum chemical calculations in ground and excited states, machine learning, statistics and data science. The proposed computational procedures are complex, require extensive fundamental and specific knowledge, ingenuity and a lot of computational work and analysis, which Dr. Romanova has brought to a successful end.

*Dr. Romanova's scientific contributions on the topic of the Habilitation Work consist of: 1) selection of molecules-chromophores, through which in the best way to reveal the relationship "topology-electronic structure (open-shell character) - potential for singlet fission"; 2) developing*

*of complex computational procedures; 3) selection of molecular descriptors; and 4) analysis of the results and the conclusions made.*

#### *Scientific contributions in the publications*

The topic of "singlet fission " has been the subject of research in three scientific publications, two of which were published in the current 2021 and one in 2020 (1, 2 and 4). Concrete results and contributions on the topic were mentioned in the analysis of the Habilitation Work, therefore only highlights will be given here. • For the first time, the relationships between the diradical character and laboratory stability in organic molecules have been identified and explained. • A computational scheme is proposed, according to which by combining quantum chemical reactivity indices and chemometric approaches, laboratory stability of organic molecules can be predicted and computational models can be developed for the discovery of new stable materials for photovoltaics. • It has been proven that molecules with a non-zero diradical character can also be laboratory stable. (1) • A comprehensive overview and analysis of molecular design strategies for singlet fission chromophores is presented. (2) • New chromophores for singlet fission have been proposed and topological rules for their molecular design have been derived. • For the first time, the stability and optical properties of boron-doped polycyclic chromophores, important in molecular design strategies, have been explained. (4)

In the other three publications on the topic "Organic molecules with an open electron shell", the following important results and contributions are obtained. • The monomers and dimeric intermediates in the polymerization of poly (p-phenylene vinylene) (PPV) by the Gilch method are modeled at various, including high levels of theory (spin-projected UHF, CASSCF, CASPT2). The calculations showed that monomers and dimeric intermediates have a diradical character, which can be associated with the kinetics and yield of by-products. (8) • New data have shown that in single-layer photovoltaic cells containing the emeraldine salt as the photoactive component, variations in the polarity of the solvent can lead to significant changes in the photo-generated *open-circuit voltage* (Voc). (12) • Unusual redox behavior of polyaniline thin porous films has been recorded and explained. (13)

Seven publications for participation in the present competition are grouped under the title "Organometallic complexes" and present a number of new data and conclusions from studies of the structure and properties of complexes of Au(I), Ru(II), Pt(II), Pd(II), Cu(II) ions with various organic ligands, which largely determine the specific application properties of the complexes. • DFT calculations and experimental results have shown that there is a dependence of the cytotoxicity of a series of Au (I) complexes on the  $\sigma$ -donor properties of the isolated ligands. (3) • On the basis of combined experimental and DFT/TDDFT studies of the optical properties of protonated and deprotonated bipyridyl complexes of Ru(II), new pH-sensitive luminescent materials have been proposed. It has been found that their luminescent properties depend mainly on the structure of the ligand and can be controlled by varying the pH. (5) • A strategy for molecular design of luminescent materials is proposed based on new mixed-ligand bipyridyl complexes of Ru(II) with pyridinyl or pyrazinyl derivatives of diazolate ligands  $[\text{Ru}(\text{bpy})_2\text{X}]^+$ . It

shows the possibility of emission in two different energy ranges (visible and IR) due to the presence of two excited states ( $^3\text{MLCT}(\text{bpy})$  and  $^3\text{MLCT}(\text{X})$ ), the energy difference of which is proportional to the energy difference of the isolated ligands LUMO levels. (6) • A relationship has been established between metallophilic interactions and the luminescent properties in Pt(II) complexes, which can be used in the design of smart luminescent materials. It has been shown for the first time that in the excited state the metallophilic interaction is determined by the ligand field. The dependence of the luminescent properties of Pt(II) complexes on the concentration is explained by the formation of excimers with a dominant metallophilic interaction. (7,9) • Absence of excited-state intermolecular interaction has been demonstrated in organometallic complexes of Pd(II) (as opposed to those of Pt(II)). The differences are explained by relativistic effects. • It has been established that in one- and two-electron oxidized forms of Pt(II) complexes, the metallophilic interaction in the ground state enhanced. The possibilities for redox-dependent change in the optical and conducting properties of the complexes in solid phase and concentrated solution are shown. (15) • The relationship between the structure and the magnetic properties of two complexes of Cu(II) (meta-Cu(acac)<sub>2</sub>(3NOPy)<sub>2</sub> and para-Cu(acac)<sub>2</sub>(4NOPy)<sub>2</sub>), which differ in topology and magnetic behavior, has been established. The obtained data on the energy, spin density distribution and MO analysis helped to propose rules for molecular design of spin-hybrid molecular magnets on the base of orbital overlap between the metal and the ligand. (14)

Two publications of Dr. Romanova are dedicated to vibroelectronic interaction. Through the studies described in them, the dependence of the vibroelectronic interaction in diradicaloids on the length of the  $\pi$ -electron conjugation was established. (11) The dependence of the vibroelectronic interaction strength in cation radicals on the parameter for correction of long-distance exchange interactions in TD-DFT methods, as well as on the type of the excited state, has been proved. (10)

The review of the publications and the topics developed gives the impression that Dr. Romanova has a deep understanding of the theory of the studied properties, processes and phenomena, has skillfully selected and applied a wide range of modern computational methods, with which she has convincingly revealed the relationship between the properties of molecules in the ground and excited states and their practical applications. In the course of her research, she has gained valuable experience for future investigations.

Dr. Julia Romanova has provided data on her teaching activity (for 3 academic years, 2018/2019, 2019/2020 and 2020/2021), for the guidance of doctoral students and research students within the scientific projects and for her activity as a scientific consultant of a bachelor's thesis and a PhD thesis. She was the editor of the Special Issue of Molecules-MDPI "Metal-Organic Complexes: Applications in Chemistry and Materials Science" (IF = 4.411).

### *Conclusion*

The research of Dr. Romanova is characterized by originality and depth of the theoretical consideration. The calculations have had a specific end goal and have led to the accumulation of a large number of valuable scientific results, which are a starting point in the design of new materials with interesting applications. In the competition for the academic position "Associate Professor",

Dr. Julia Romanova has presented a sufficient number of original scientific papers published after acquisition of "Doctor" degree. The results achieved by the candidate fully comply with the Law for development of the academic staff in Republic of Bulgaria and the Recommended Criteria of the Faculty of Chemistry and Pharmacy, Sofia University. Dr. Romanova is a very successful and enthusiastic young researcher who has an indisputable scientific qualification and potential for research in the field of theoretical chemistry and computational material science. After the analysis of the materials presented for the competition, I find it reasonable to give my positive assessment by voting convincingly "yes" for the election of Dr. Julia Ruslanova Romanova to the academic position of "Associate Professor" at the Faculty of Chemistry and Pharmacy, Sofia University in Professional field 4.2. "Chemical Sciences", scientific specialty "Theoretical Chemistry".

Sofia, November 17, 2021.

Reviewer:

(Natasha Trendafilova, Prof. Dr. IGIC-BAS)