REVIEW

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on the materials submitted for participation in a competition for the academic position of **"professor",** announced at the Institute of Optical Materials and Technologies "Acad. Jordan Malinowski" - BAS (IOMT-BAS) in the professional field 4.2 Chemical Sciences (Physical Chemistry).

1. General Presentation

By order No. PD-15-305 of 14.05.2025, issued by the Director of IOMT-BAS, I have been appointed as a member of the scientific jury of a competition for the academic position of "professor" for the needs of the field of "Optical Metrology and Holography".
In the competition for "professor," announced in the State Gazette, issue 24 of 21.03.2025, **Assoc. Prof. Dr. Silvia Emilova Angelova** appeared as the only candidate.

1. Brief biographical data of the candidate

Associate Professor Dr. Silvia Angelova graduated from the Faculty of Chemistry and Pharmacy of Sofia University "St. Kliment Ohridski", in chemistry, in 1995 and she is pursuing postgraduate training in Business Management and Marketing at the Institute for Postgraduate Training at the University of National and World Economy.

She prepared her doctoral dissertation on the topic "Quantum-chemically calculated NMR parameters as a tool for studying tautomeric and conformational transformations" at the Institute of Organic Chemistry with a Center for Phytochemistry, Bulgarian Academy of Sciences (IOCFC-BAS) and defended it in 2009 before the Higher Attestation Commission in professional field 4.2. Chemical Sciences, specialty: Theoretical Chemistry.

In the period from 1996 to 2019, Assoc. Prof. Angelova worked at the Institute of Organic Chemistry with a Center for Phytochemistry of the Bulgarian Academy of Sciences, successively holding the positions of chemist, research associate, assistant and chief assistant. She conducted a postdoctoral specialization at the University of Alcalá, Alcalá de Henares (Madrid), Spain from March 2012 to March 2013.

In 2019, after winning a competition to occupy the academic position of "associate professor", she moved his place of work to the Institute of Optical Materials and Technologies - BAS, where since 2022 she has served as Scientific Secretary and currently leads a group of 3 young researchers working in the field of computational chemistry.

The main scientific and research interests of Assoc. Prof. Dr. Angelova are in the field of theoretical chemistry: quantum chemistry, computational chemistry and molecular modeling.

2. Research activity

A) The overall research activity of Assoc. Prof. Silvia Angelova includes co-authorship in 112 publications and one independent publication, presented in a list. 101 of the articles can be found in the Scopus database and, when consulted, currently provide her with an h-index of 13 (Scopus, without self-citations). Part of the results in these publications were also obtained in the implementation of 19 research and educational projects, of which 7 are with the Bulgarian Science Fund (BSF) under calls for fundamental scientific research, 4 are under bilateral cooperation agreements of Bulgaria (BSF) with foreign countries (Italy, Macedonia, Austria, Russia), 4 are bilateral cooperation of the Bulgarian Academy of Sciences with various scientific institutions abroad, 1 is under the Operational Program "Science and Education for Smart Growth", 1 is in implementation of the National Plan for Recovery and Sustainability, 1 is international with the National Research Fund of Switzerland, and 1 is under the student internship program of the Ministry of Education and Science. One of the ongoing fundamental research projects is being implemented under the guidance of the candidate.

B) The results of the scientific research activity **with which the candidate participates in the announced competition for the position of "professor" are** summarized and described in 19 scientific publications, all in journals with ISI "impact factor". In terms of quartiles, 10 of publications are in journals with quartile Q1, 7 with Q2, 1 with Q3, 1 without quartile of the journal in the year of publication, which is evidence of the high scientific level of the research described in these publications. Among the journals, the renowned ones in the field of physicochemical research of materials stand out: *Physical Chemistry Chemical Physics* with IF_{2017} =4.49, *ChemPhysChem* with IF_{2011} =3.412, in the field of organic chemistry and dyes *Dyes and Pigments* with IF_{2017} =3.767, and also *Antioxydants* with IF_{2021} =7.675.

The candidate is the first author in 4 publications [19,40,58,109], the last (leading) author in 3 [70,104,105], the corresponding author in 8 [19,58,59,60,70,73,75] and 1 publication is independent [59].

The publications, citations and conference participations of Assoc. Prof. Dr. Silvia Angelova selected for the competition provide the necessary points corresponding to the minimum national requirements reflected in the Regulations for the Implementation of the Act on the Development of the Academic Staff in the Republic of Bulgaria, as well as in the Regulations of the Institute of Optical Materials and Technologies - BAS and exceed them in most of the indicators. For example, under indicator 4, 165 points are presented with a minimum of 100 points for participation in the competition, under indicator 7: 245 points with a minimum of 220, under indicator 11: 170 with a minimum of 120, under indicators 13 – 18: 280 with a required 150.

The publications presented in this competition differ from those presented in the candidate's dissertation for the acquisition of the PhD degree and from those with which she participated in the competition for the academic position of "associate professor".

According to the requirements of the competition for the academic position of "professor", the submitted publications are divided into two groups:

I. Scientific publications equivalent to **habilitation thesis** (group of indicators "B", indicator "4"): 7 issues (by number from the general list 68, 69, 84, 85, 97, 100, 104)

II. Scientific publications outside the habilitation thesis (group of indicators "G", indicator "7"): 12 issues (by numbers from the general list 15, 19, 40, 43, 58-60, 70, 73, 75, 105, 109);

In terms of thematic content, the publications from the habilitation report could be divided into the following 3 areas, where the candidate's respective main contributions are also formed, as she herself presents them in the report on the author's contributions:

(1) Application of quantum chemical calculations to study the ground state electronic structure and properties of chemosensory systems based on 1,8-naphthalimides and rhodamine [68, 69, 84, 97, 100].

The largest group of publications in the habilitation thesis is concentrated in this topic. Some of them are devoted to quantum-chemical studies of dyes, derivatives of 1,8-naphthalimide [68, 97, 100], which allow to determine their electronic structure. The interest in these compounds is due to their antibacterial, antifungal, anticancer and antiviral properties, which determine their biological and medical applications. At the same time, the relatively low molecular weight, compact molecule and the possibility of introducing active groups capable of participating in polymerization processes make these compounds suitable for structural modification of polymeric materials and as photoinitiators of free-radical polymerization upon irradiation with visible light. Derivatives of 1,8-naphthalimide have been studied as sensor systems for detecting cations, anions or neutral pollutants released into the environment during a number of production processes. The topic is closely related to overcoming serious environmental problems and is undoubtedly relevant, both from a fundamental and applied perspective.

The contribution of the studies reflected in this topic consists in calculations performed using the methods of density functional theory (DFT) and time-dependent density functional (TD-DFT) of two newly synthesized derivatives of 1,8-naphthalimide (NI1 and NI2) , which allow to study the geometry and electronic structure of these systems, including the influence of different organic solvents on the absorption spectra, protonation and the ability of these systems to form complexes with metal cations (specifically Mg^{2+} and Fe^{3+}) in order to explain the influence of different metal ions on the photophysical characteristics [97]. Another derivative of 1,8-naphthalimide (4-(4,6-diamino-1,3,5-triazin-2'-ylamino)-N-(2-dimethylaminoethyl)-1,8-naphthalimide, NI-DAT) has been studied as a sensor for Hg^{2+} [100]. Here, modeled complexes of a model system, representing a fragment of the molecule, with Hg^{2+} and Mg^{2+} , are used to explain the experimentally observed selective sensing ability of the studied compound.

The structure of two dyes (NI3 and NI4), one of which is new (NI3) [68], was also studied using computational methods, after combining the sensing activity of 1,8-naphthalimides and their ability to copolymerize with traditional monomers used in polymer chemistry (vinyl and methacrylate monomers) to obtain polymers with sensing fragments incorporated in the side chain. The influence of the solvent on the spectral properties of the two compounds, the charge distribution, protonation and the formation of complexes with metal cations were studied in detail to interpret the sensing ability of the two chromophore systems. After demonstrating sensing activity, the sensing fragments based on the two naphthalimides were used to prepare fluorescent copolymers with styrene.

An important result is the incorporation of 1,8-naphthalimides into polypropyleneamine (PPA) and polyaminoamine (PAMAM) dendrimers of different generations, which resulted in new fluorescent dendrimers with unique properties. Due to the large size of these systems, in the study of one such peripherally modified with 1,8-naphthalimide (3-(6-nitro-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)propanoic acid) PAMAM dendrimer (D1) [69], a fragment of the system was modeled, for which the geometry in the ground state was optimized and possible interactions with explicit solvent molecules (methanol) were considered, since hydrogen bonds with solvent molecules are decisive for the 3D structure of the dendrimer. The preferred protonation sites were identified and the UV spectra were theoretically predicted. The compounds were investigated for antimicrobial and cytotoxic activity in the free state and after application to the surface of cotton fabric.

Rhodamine dyes possess unique optical properties and are widely used in biotechnological applications (fluorescence microscopy, flow cytometry, fluorescence correlation spectroscopy, etc.). Rhodamines are characterized by interconversion between non-fluorescent and fluorescent forms. On the other hand, pyrazoles possess significant chelating ability, which provokes the synthesis of a chemosensor containing both fragments [84]. The geometries of both forms of RhPzNH2 have been optimized and complexes with hydrated and non-hydrated Cu^{2+} ions have been modeled at dye-metal stoichiometry 1:1 and 2:1, with positioning of the metal cation at different ligating groups. In the absence of experimental data confirming the exact location of the metal and the structure of the complex, molecular modeling data are the only source of such information. The properties of the compound as a molecular logic device have been investigated and it has been found that it acts as a digital comparator.

(2) Application of quantum chemical calculations to the study of host-guest complexes of dyes and cucurbit[7]uril [104]

In this publication, quantum chemical calculations are applied to solve the problem of dye incorporation into a host molecule and the creation of stable complexes. Five dyes traditionally used in laser systems (Pyridine 1, Pyridine 2, Rhodamine 6G, Rhodamine B, Rhodamine 700) are selected as the guest and a cucurbit[7]uril molecule [104] as the host. By analogy with host-guest systems described in the scientific literature, such complexes are expected to exhibit improved photophysical properties, increased photostability, provide higher fluorescence quantum yield and be of interest for modeling and optimization of fluorescent materials.

Since the cavity of the host system is not large enough to accommodate the entire dye molecules, it is necessary to model complexes in which different fragments of the guest molecules are inside the CB[7] cavity. The process has been studied in the gas phase and taking into account the influence of the environment, using an implicit solvent ($CHCl_3$ and DMSO). It has been demonstrated that quantum-chemical (DFT) calculations can predict the interaction of the host molecule with the dye molecules from a thermodynamic point of view. The thermodynamically favorable inclusion of the studied laser dyes in the CB[7] cavity will affect their photophysical properties by improving their photostability, limiting the interaction with the environment (and possibly quenching of fluorescence). Furthermore, the confinement of dye molecules in the CB[7] cavity is likely to reduce non-radiative decay pathways, leading to an increase in the fluorescence quantum yield. These effects make CB[7] an

attractive encapsulating agent for applications in laser technology and other photonic devices where stable and highly fluorescent materials are required. It is important to note that polymer side chains can also be incorporated into the CB[7] cavity, and this interaction should be taken into account when designing supramolecular polymer hydrogels using cucurbiturils (CB-SPHs). The differences in the efficiency of the incorporation reactions at different orientations of the dye molecules (leading, respectively, to different ways of incorporating the guest molecules into the cavity of the host molecule) show that it is of utmost importance to assess which parts of the molecule should remain free for subsequent treatment with CB[7] in cases where the dye is covalently bound to the polymer, in order for the interaction to take place and the desired effect to be achieved. **The main contribution** of the conducted entirely theoretical study is the obtained useful new structural data and the outlined design guidelines for supramolecular systems based on dyes and CB[7], which have potential applications in current and rapidly developing fields such as photonics and materials science.

(3) Application of quantum chemical calculations to study the ground state electronic structure and properties of D-A+(D) chromophores for nonlinear optical applications [85].

The aim of this study is to obtain new charged donor-acceptor (D-A+) chromophores with quinolizinium cations as the acceptor moiety by treating haloquinolizinium salts with N-heteroarylstannates under Stille reaction conditions [85]. The approach used provides easy access to potential one-dimensional D-A+ and two-dimensional D-A+-D chromophores, in which the acceptor moiety (A+) is an azonium cation and the donors are various π-electron-rich N-heterocycles. These systems were generated by direct coupling of the donor and acceptor moieties (without a conjugated system between them), which is unusual for compounds exhibiting promising nonlinear optical properties, but despite the lack of a linear connection between D- and A+, the nonlinear activity does not decrease, but even increases. Experimentally (by Hyper-Rayleigh Scattering (HRS)) it has been found that some chromophores reach very high values of first hyperpolarizability. The electronic structures and properties (including linear and nonlinear optical properties) of quinolizinium chromophores have been investigated by theoretical (DFT, HF and MP2) calculations. Theoretical calculations have been used to study the influence of substituents (and protecting groups) in the chromophore system on the optical properties of the dyes. The energies of the HOMO and LUMO orbitals, as well as the differences between them (HOMO–LUMO gap, HLG) have served to characterize the structure. As a result of the combined experimental and theoretical study, a promising strategy for the rational design of directly connected DA building blocks for the creation of new nonlinear optical materials on an organic basis has been proposed.

II. Contributions to scientific publications in addition of the habilitation thesis (group of indicators "Г", indicator "7").

The twelve publications included in this group concern the application of computational methods to the study of the structure and properties of organic compounds and complexes. They illustrate a wide range of scientific problems for the solution of which computational methods have been used (alone or in combination with experiments). In quantum-chemical calculations, a wide range of DFT functionals has been used: B3LYP [15,19,58,59,60,70,73], M06 [58], M062X [40,58,75], MN12-SX [75], ωB97XD [105] and P BE0 for TDDFT

calculations [19,60], and in some cases - more than one DFT functional, as well as ab initio calculations [19].

The processes of isomerization [15,58,60], tautomerization [19,43,58,75], aggregation [19,105], formation of complexes with metal cations, water molecules, etc. [40,59,60,70,105,109] and homolytic cleavage of the O-H bond [73] have been studied. The listed processes often occur in solution and studies related to the influence of the solvent on the equilibrium are of great importance due to the fact that the structure (and reactivity) of the molecule can be quite different in a solvent environment. Methods for taking into account the influence of the solvent as a dielectric (implicit methods) have been used in almost all publications of this group: PCM (Polarizable Continuum Model) in publications [19,43,58,60,75] and SMD (Solvation Model based on Density) in publications [40,59,70,105,109].

When solving specific scientific problems in some of these studies, it was sufficient to optimize the geometry of one or more molecules/ions, but in most cases it was necessary to predict various characteristics - such as energies of the HOMO and LUMO orbitals, as well as the differences between them (HOMO–LUMO gap, HLG), charges, chemical shifts and spin-spin interaction constants, simulation of UV spectra, etc., calculation of various thermodynamic parameters (bond dissociation enthalpy, enthalpies and Gibbs energies in aggregation reactions and/or host-guest complex formation).

In general, the candidate's contributions are mainly in the planning and carrying out of the calculations of the electronic structure of the studied systems and finding a correlation with experimental data (if available in the scientific literature or measured) for some of their properties (sensory, optical, chemical) and those predicted by the applied computational models. Processes occurring in the studied systems such as isomerization, tautomerization, complexation, etc. were also monitored.

3. Teaching and expert activities

In accordance with her competencies, Assoc. Prof. Silvia Angelova leads a course of lectures for doctoral students on the topic "Computer modeling of molecular structure and optical properties of single molecules and supramolecular aggregates" at the Training Center of the Bulgarian Academy of Sciences with a teaching load of 30 hours. She actively participates in the training of graduates, having been co-supervisor of 11 bachelors' and 5 masters' theses. She is a reviewer of project proposals in various competitions of the Bulgarian National Science Fund, of manuscripts submitted to renowned scientific journals for publication, of competitive procedures for awarding degrees and occupying academic positions, etc.

4. Critical notes and recommendations

I have no critical remarks towards the candidate. I would only like to comment that in the reference for fulfilling the minimum requirements, the quartiles of the journals should be determined by the citation rank of the journal by impact factor (JCR-IF), and not by the citation index (JCI) . In the data presented by the candidate for most articles, the quartiles of the journals are presented according to the impact factor, but there are also quartiles determined according to the citation index for 2 of the publications:

#1 of the habilitation thesis - Staneva, D., Angelova, S., Grabchev, I., Spectral Characteristics and Sensor Ability of a New 1,8-Naphthalimide and Its Copolymer with Styrene. Sensors, 2020, 20, 12, 3501, DOI: https://doi.org/10.3390/s20123501. ISSN: 14248220, Q1 (JCI)
#6 from group "Г" - Angelova, S., Complexation of IA and IIA group metal ions by N-phenylaza-15-crown-5 containing Schiff bases: A DFT study, Inorganica Chimica Acta, 2019, 487, 316-321, DOI:https://doi.org/10.1016/j.ica.2018.12.041. ISSN: 00201693, 18733255 , Q1 (JCI)

For the first publication, the check showed that there is an area in which the quartile is Q1 and according to the impact factor, which corresponds to the Regulations for the Implementation of the ADASRB is enough for it to receive 25 points, but for the second one, the quartile by impact factor is Q2 for the year of publication 2019 and the points for this publication should be 20, which will make the total number of points by indicator "Г" 240, instead of 245, but it will still exceed the minimum threshold of 220 points.
Considering the interesting, significant and useful results of the computational methods and theoretical calculations reflected in the publications presented in the competition, I wish Assoc. Prof. Angelova to continue to work as thoroughly and persistently in her field of qualification and to develop her existing and also new collaborations with various research groups.

CONCLUSION

The presented by the candidate in the competition, **Assoc. Prof. Dr. Silvia Emilova Angelova,** fully comply with the requirements of the Act on the Development of the Academic Staff in the Republic of Bulgaria, the Regulations for its implementation and the relevant Regulations of the Bulgarian Academy of Sciences and the Institute of Optical Materials and Technologies, as well as the topic of the announced competition for "professor".
While, I highly appreciate the contributions of the presented in the competition works and activities, **I fully convincedly give a positive assessment** and recommend to the esteemed members of the Scientific Jury to prepare a report with a proposal to the Scientific Council of IOMT, Assoc. Prof. Dr. Silvia Emilova Angelova to be elected to the academic position of "professor" in professional field 4.2. Chemical Sciences (Physical Chemistry) at the Institute of Optical Materials and Technologies - BAS.

11.07.2025

Reviewer: .....
prof. Dr. Daniela Karashanova