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Theoretical Studies and Computer Modeling of Supramolecular Chemical Systems: Structure, Properties and Reactivity †

Alexander S. Novikov [1,2,3,*]

[1] Saint Petersburg State University, Universitetskaya Nab., 7/9, Saint Petersburg, 199034, Russian Federation
[2] ITMO University, Kronverksky Pr., 49, Bldg. A, Saint Petersburg, 197101, Russian Federation
[3] Peoples' Friendship University of Russia (RUDN University), Miklukho-Maklaya St., 6, Moscow, 117198, Russian Federation
* Correspondence: a.s.novikov@spbu.ru
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Abstract: The results of my research in fields of theoretical studies and computer modeling of supramolecular chemical systems were presented. The main attention was focused on theoretical studies in the following topics: cycloaddition and nucleophilic addition reactions involving substrates with multiple CC and CN bonds, their mechanisms, driving forces, kinetics and thermodynamics; consideration of the catalysis of hydrocarbons oxidation processes and their conversion to alcohols, ethers, aldehydes, ketones and carboxylic acids; investigations of various unusual types of non-covalent interactions (from quite trivial hydrogen bonds to more exotic σ-hole, π-hole and metallophilic interactions) in organic, organometallic and coordination compounds. Some fundamental issues of supramolecular chemical systems were also discussed (e.g., structure and properties of chemical compounds and their supramolecular associates; conformational transitions and rotation barriers of functional groups; nature of chemical bonds, orbital and charge factors; photophysical properties).

Keywords: coordination chemistry; organometallic chemistry; inorganic chemistry; organic chemistry; quantum chemical calculations; computer modeling; supramolecular systems; catalysis; reactivity

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In this Keynote presentation, I have presented results of my research in fields of theoretical studies and computer modeling of supramolecular chemical systems. The main attention was focused on theoretical studies in the following topics: cycloaddition and nucleophilic addition reactions involving substrates with multiple CC and CN bonds (viz. metal-assisted (by Au(I), Au(III), Pt(II), Pt(IV), Re(V), and Pd(II)) 1,3-dipolar cycloaddition of aldo- and ketonitrones to isocyanides [1]; Cu(I)-catalyzed 1,3-dipolar cycloaddition of ketonitrones to dialkylcyanamides [2]; nucleophilic addition of hydroxyguanidines, amidoximes, and ketoximes to nitrilium *closo*-decaborate clusters [3]; nucleophilic addition of amidoximes to aromatic nitrile complexes *trans*-[$PtCl_2(RC_6H_4CN)_2$] (R = *p*-CF_3, H, *o*-Cl) [4]), their mechanisms, driving forces, kinetics and thermodynamics, and correlations between activation and reaction energies and the calculated unscaled stretching vibration frequencies of CN group in metal-free and coordinated isocyanides were also discussed [5]; consideration of the catalysis of hydrocarbons oxidation processes and their conversion to alcohols, ethers, aldehydes, ketones and carboxylic acids (mechanisms of the rate-limiting stages of alkanes oxidation and olefins epoxidation with hydrogen peroxide assisted by the formation of hydroxyl radicals, catalyzed by aqua complexes $[M(H_2O)_n]^{3+}$ of the group III metals exhibiting a unique stable non-zero oxidation state (M = Ga, In, Sc, Y, or La) [6]); investigations of various unusual types of non-covalent interactions (from

quite trivial hydrogen bonds to more exotic σ-hole, π-hole and metallophilic interactions) in organic, organometallic and coordination compounds (viz. intermolecular hydrogen bonds and anagostic interactions in Pd(II) acyclic diaminocarbene complexes [7]; supramolecular polymers derived from Pd(II) and Pt(II) N,N-diaryldiazabutadiene Schiff base complexes via C(sp^2)–H···Hal hydrogen bonding [8]; halogen bonds with metal centers [9] and isocyano carbon atom [10]; non-covalent B–H···π(Ph) interactions determines stabilization of the configuration around the amidrazone C=N bond in *closo*-decaborato amidrazones [11]; effect of halogen bonding on solubility of Pd/Pt isocyanide complexes [12]; chalcogen bonds in Pd(II) carbene complexes [13]; stacking interactions and π-hole interactions in transition metal complexes and various supramolecular building blocks [14]; ligation-enhanced π-hole···π, π-hole···metal center, and π-hole···lone pair interactions involving isocyanides [15]; reverse arene sandwich structures based upon π-hole···[M(II)] (d^8 M = Pt, Pd) interactions intramolecular [16]; xenon derivatives as aerogen bond-donating catalysts for organic transformations [17]; sulfonium and selenonium salts as noncovalent organocatalysts for the multicomponent Groebke−Blackburn−Bienaymé reaction [18]). Some fundamental issues of supramolecular chemical systems were also discussed (e.g., structure and properties of chemical compounds and their supramolecular associates (viz. comprehensive theoretical study of the aminonitrone-iminohydroxamic acid tautomerism [19]; melamine–barbiturate supramolecular assembly as a pH-dependent organic radical trap material [20]); conformational transitions and rotation barriers of functional groups; nature of chemical bonds, orbital and charge factors; photophysical properties of phosphorescent Pt(II) complexes featuring chelated acetoxime pyrazoles [21]). This research is interdisciplinary in nature and lies at the intersection of computer modeling with such natural science disciplines as chemistry, physics, crystallography, biology, and medicine, as well as directly related to materials science and nanotechnology. The results obtained in the course of this research can be promising for finding new original ways to create high-tech functional materials with valuable mechanical, magnetic and optical properties, porous structures with a developed surface, sensors, battery cells, liquid crystals; synthesis of antibacterial, antiviral and antineoplastic drugs, labels for neutron capture therapy of oncological diseases; catalysts for cross-coupling processes (for example, the Suzuki, Heck and Sonogashira reactions) and the conversion of hydrocarbons (for example, to alcohols, epoxides, ethers, aldehydes, ketones and carboxylic acids), as well as multicomponent reactions.

For list of my publications see Scopus ID: 50262902200, Web of Science ResearcherID: L-5001-2015, and https://scholar.google.com/citations?hl=en&user=n_rBOQcAAAAJ.

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