Ministry of Education and Science of the Republic of Kazakhstan.
L.N. Gumilyov Eurasian National University.
Department - Technical Physics.
Speciality 5B072300 - "Technical Physics".

Determination of optical properties of pentacoordinated silicon complexes using DFT method

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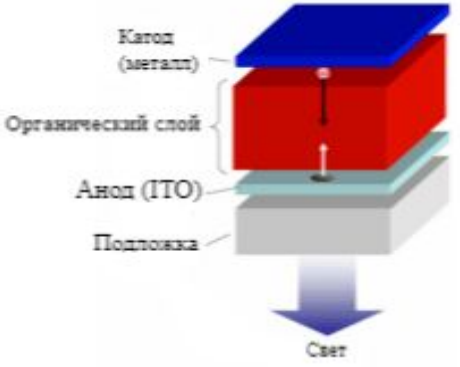
Relevance

In recent years, there has been a steady interest in the development of new materials for organic electronic devices. Accordingly, the study of electron transfer processes in organic molecules and coordination complexes with organic ligands meets the modern needs of microelectronics development in Kazakhstan.



Aims and objectives of the study

Aim - To define the optical properties of pentacoordinated silicon complexes using DFT method.

Objectives - To conduct quantum chemical calculation using DFT method; to investigate of the optical properties of the complex Si(pincer)2 ; to determine the charge dependence of the Si complex(ttpy)2 from its electrochromic response; to compare the obtained results with known experimental data, which were got by American scientists.

Theoretical significance

The research uses a method DFT that allows to get more reliable data.

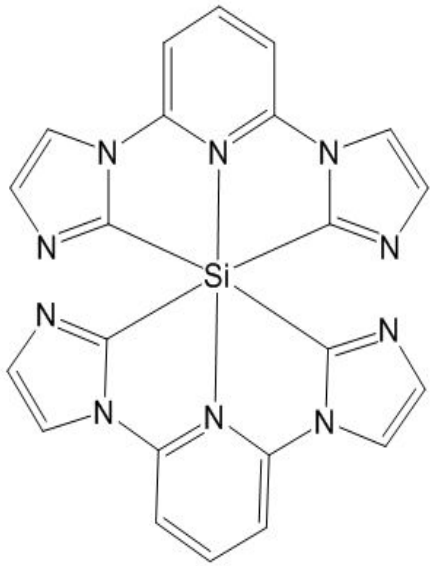
Practical significance

The results of the research show that silicon pentacoordination complexes represent a promising new class of metallochelates for organic electronic devices in Kazakhstan. That means, they can be used as candidates for transporting charge and/or electroluminescent materials in organic electronic devices.

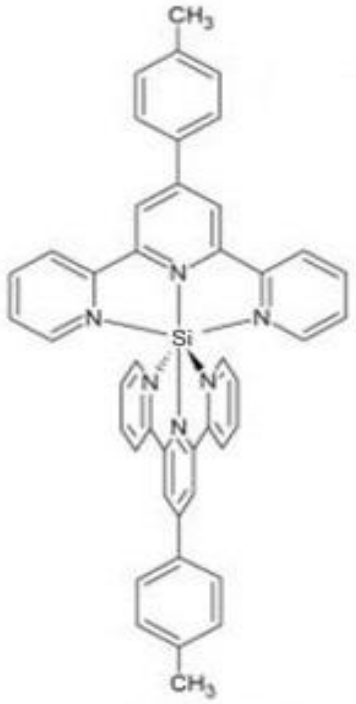
The object and subject of the study

Object - Pentacoordinated silicon complexes.

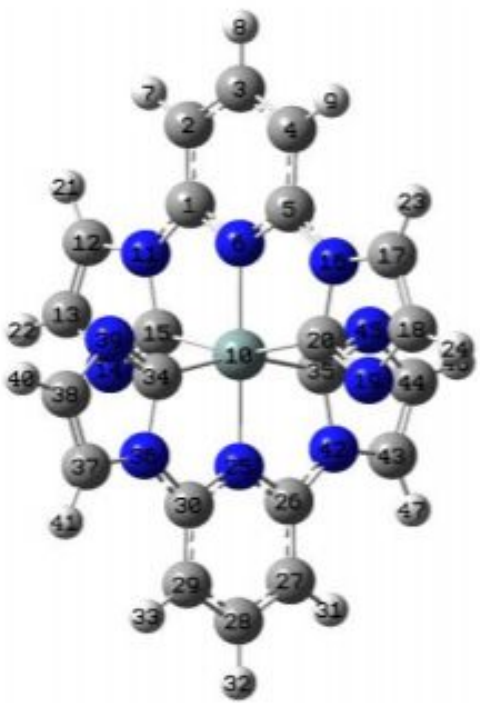
Subject - A study of optical properties and quantum-chemical calculations of silicon pentacoordinated complexes with ligands by the DFT method.

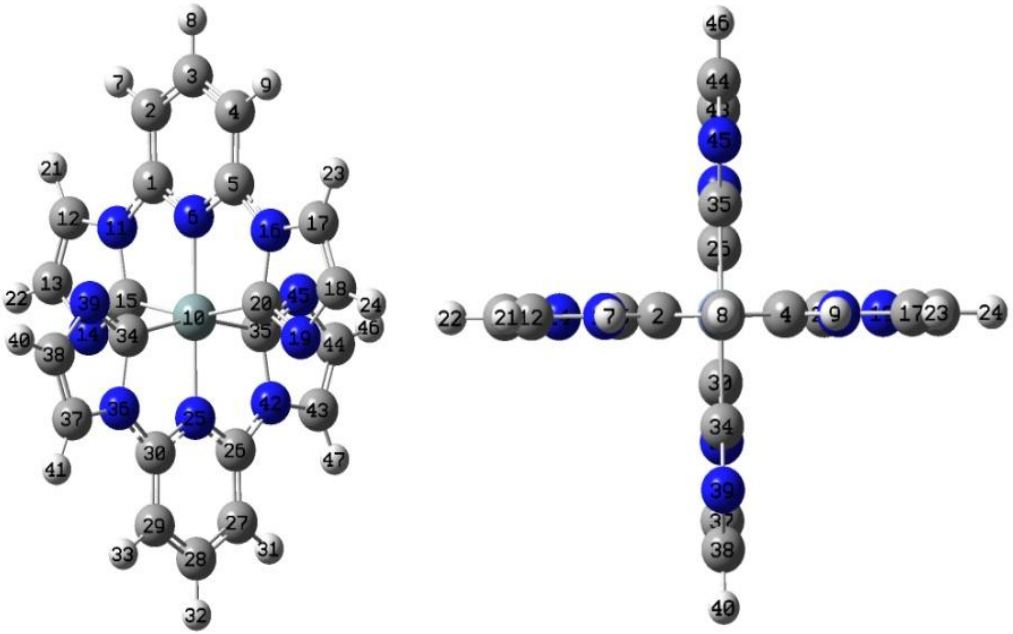


Chemical structure of the pentacoordinate complex Si[(pincer)2]0

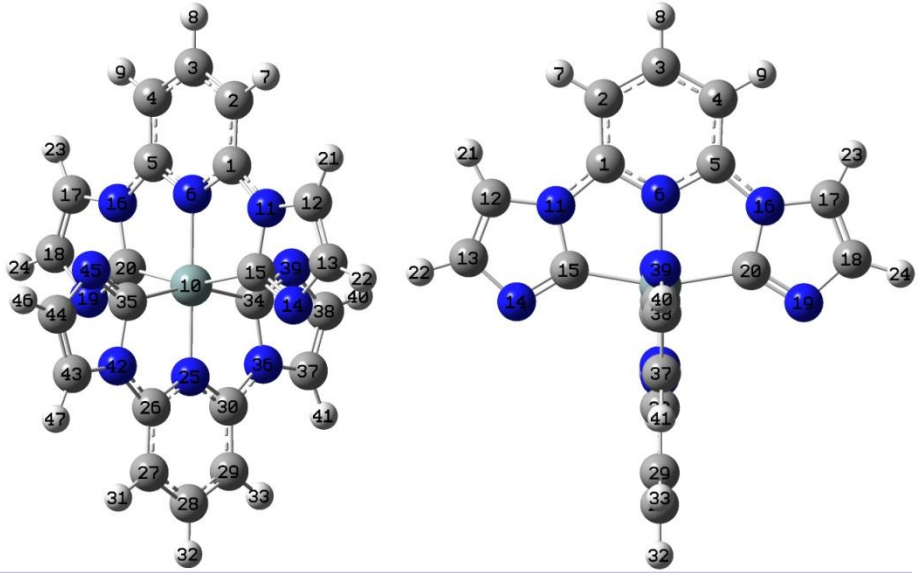


Chemical structure of the pentacoordinate complex Si[(ttpy)2]+n

Структура Молекулярная формула	Модель структуры	(Å) Длина связей		(°) Углы связей	
$Si[(pincer)2]^0$ $C_{22}H_{14}N_{10}Si$		Si^{10}-N^6 Si^{10}-C^{20} N^6-C^5 C^5-N^{16} N^{16}-C^{20} N^{16}-C^{17} C^{17}-C^{18} C^{18}-N^{19} N^{19}-C^{20} C^5-C^4 C^4-C^3 C^3-H^8	1.956 1.971 1.344 1.380 1.411 1.390 1.365 1.390 1.313 1.395 1.396 1.086	N^6-Si^{10}-N^{25} N^6-Si^{10}-C^{20} C^{20}-Si^{10}-N^{25} Si^{10}-N^6-C^5 Si^{10}-C^{20}-N^{16} N^6-C^5-C^4 C^5-C^4-C^3 C^4-C^3-C^2 N^{19}-C^{20}-N^{16} C^{20}-N^{16}-C^{17} N^{16}-C^{17}-C^{18} C^{17}-C^{18}-N^{19}	180.000 80.418 99.582 118.603 111.454 120.339 117.144 122.240 109.263 108.160 104.369 111.564



Theoretical modelling of the Si(pincer)2 structure has been performed using a functional and basis set based on a combination of the Hartree-Fock method and density functional theory using the Becke-Lee-Yang-Parr exchange-correlation potential.

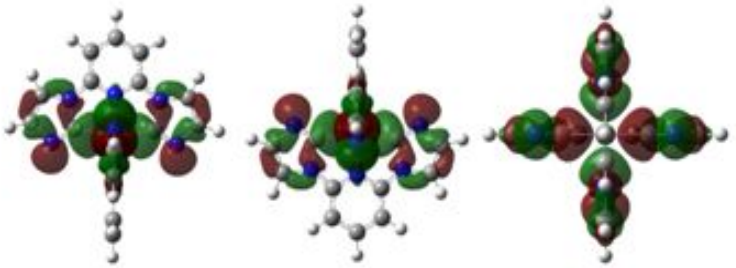


Optimised structure of Si(pincer)2 molecule by the B3LYP method

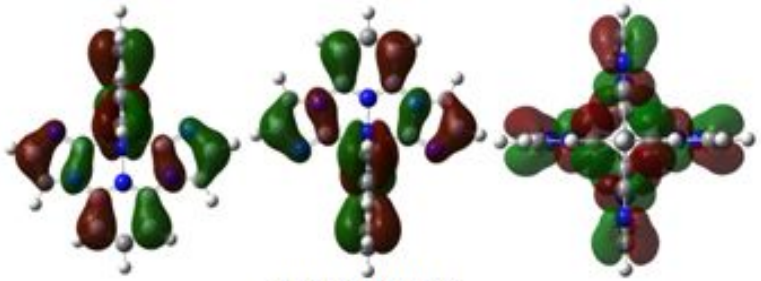
TD-DFT calculations reproduce the observed electron spectrum

Electron absorption spectrum graph for [Si(pincer)2]0 structure

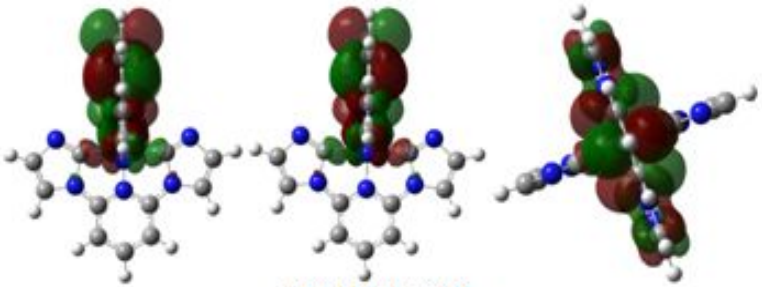
MO 107(HOMO-8)



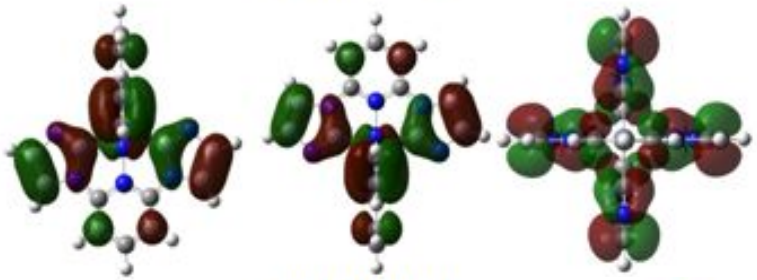
MO 115 (HOMO)



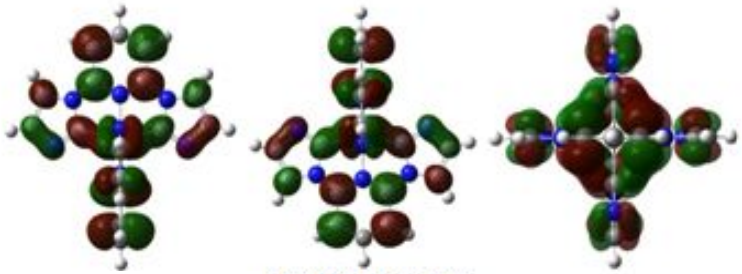
MO 111(HOMO-4)



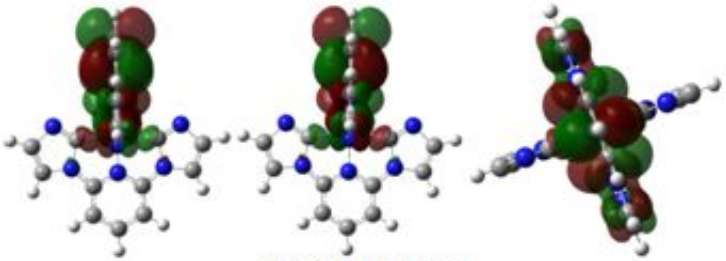
MO 116 (LUMO)



MO 114 (HOMO-1)



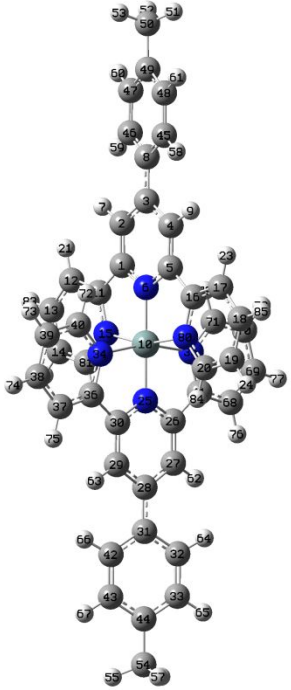
MO 118 (LUMO+2)

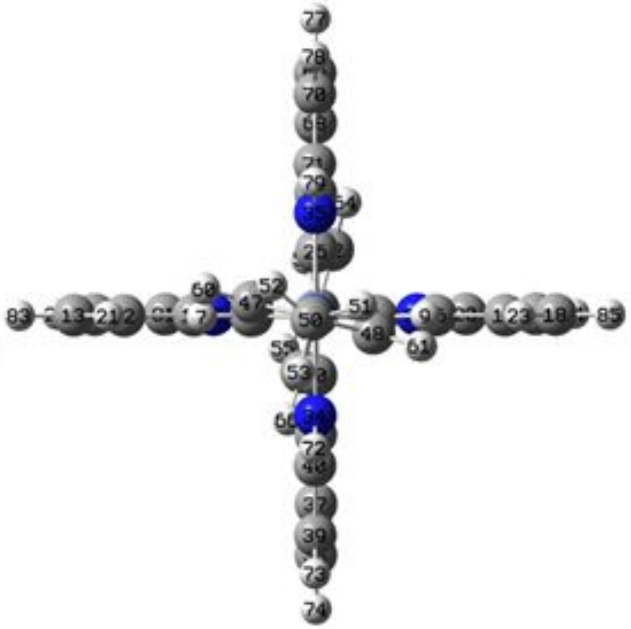


MO 117 (LUMO+1)

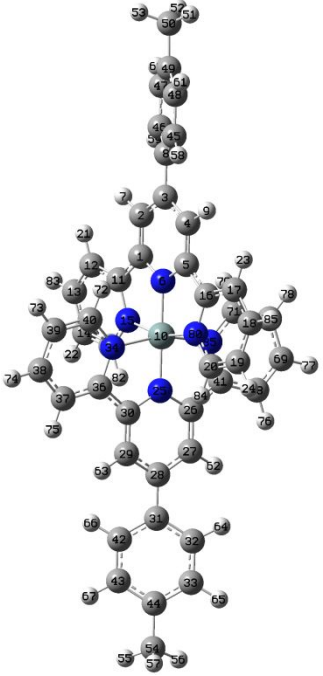
HOMO - Highest occupied MO
LUMO – Lower unoccupied MO

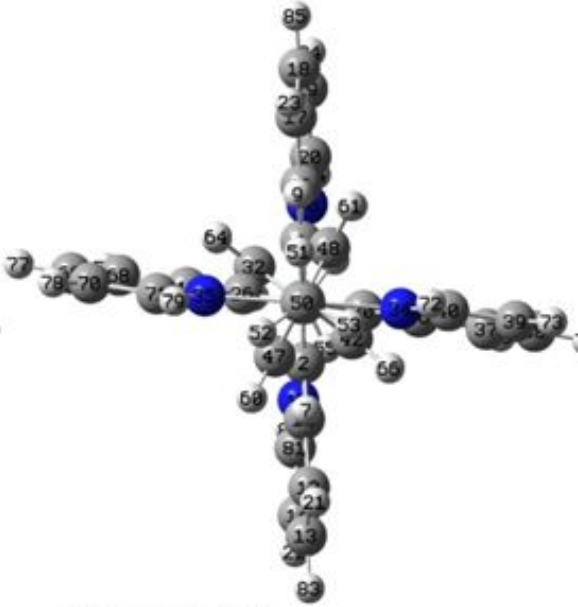
Molecular orbitals involved in intensive transitions of the [Si(pincer)2]0 structure



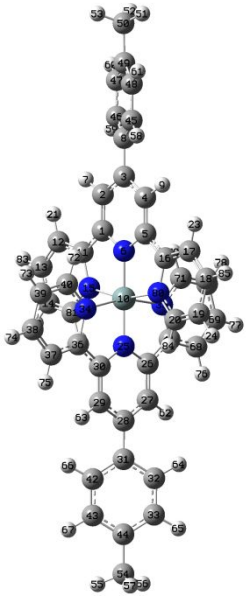


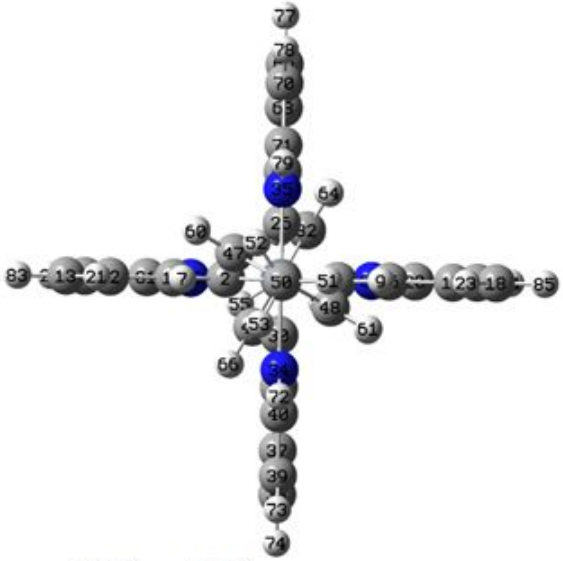
Si[(ttpy)2]$^{+4}$





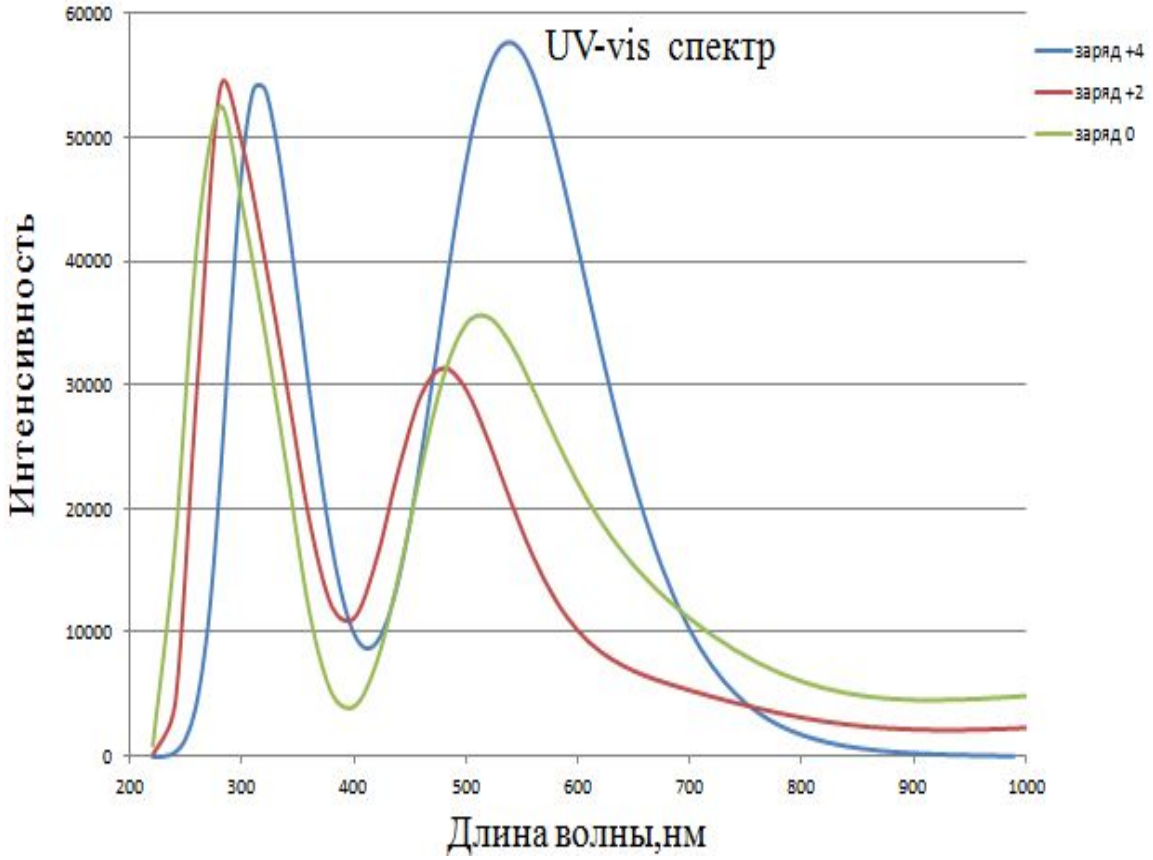
Si[(ttpy)2]$^{+2}$



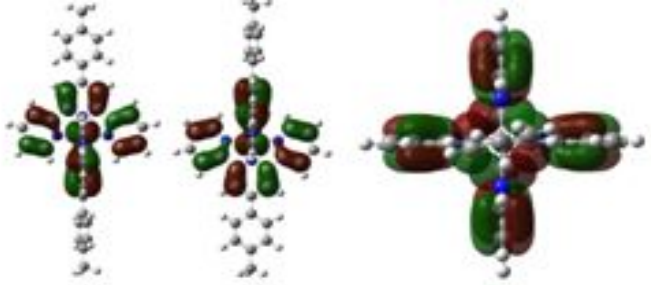


Si[(ttpy)2]^{0}

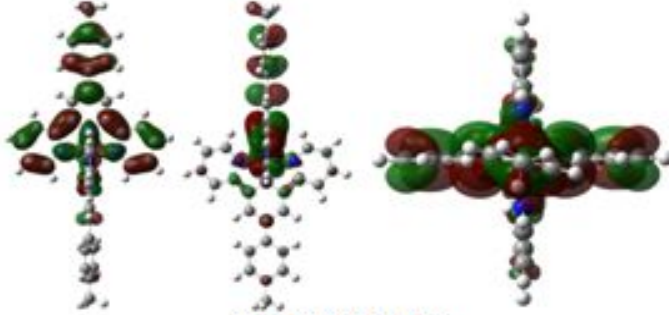
Finite fully optimised structures Si[(ttpy)2]+n



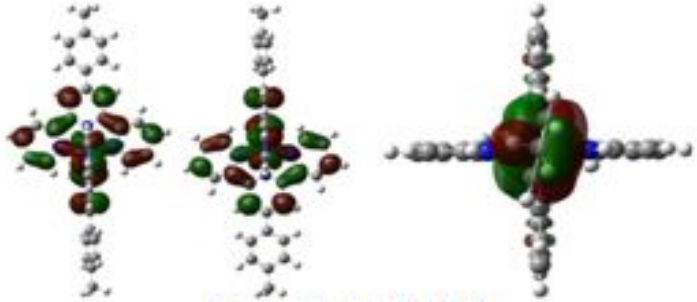
Electronic absorption spectra of the complex [Si(ttpy)2]+n :
blue line, n = 4 ;
red line, n = 2 ;
green line, n = 0



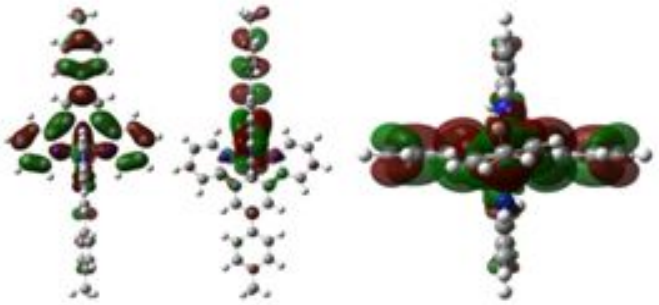
MO 170 (HOMO-5)



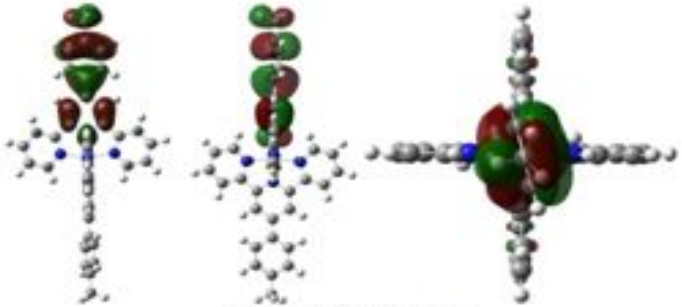
MO 176 (LUMO)



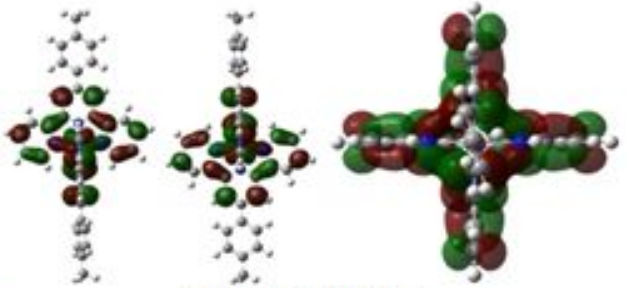
MO 174 (HOMO-1)



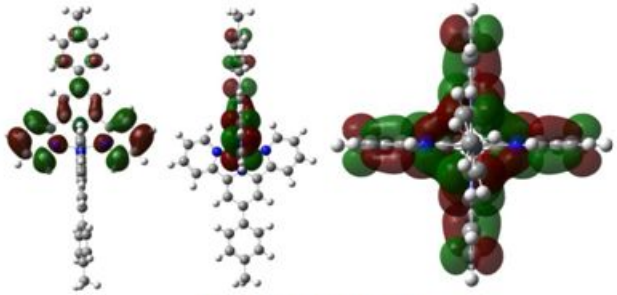
MO 177 (LUMO+1)



MO 175 (HOMO)

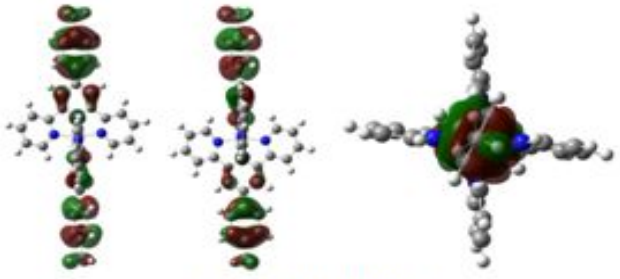


MO 178 (LUMO+2)

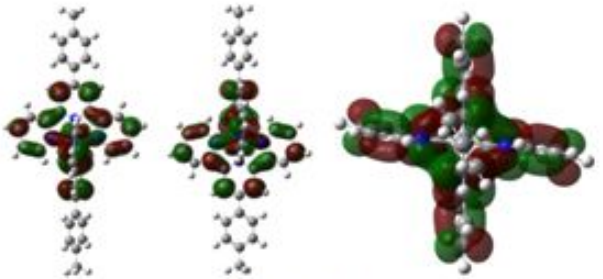


MO 181 (LUMO+5)

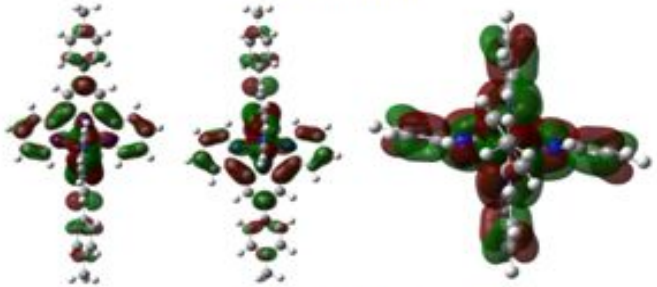
Molecular orbitals involved in intensive transitions of the [Si(ttpy)2]+4 structure



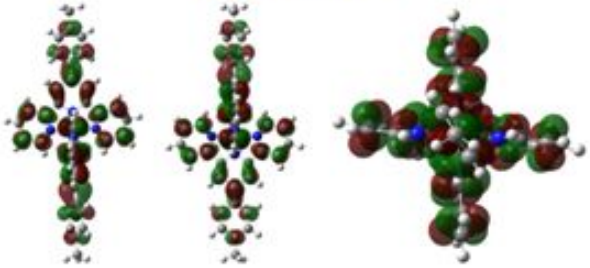
MO 174 (HOMO-2)



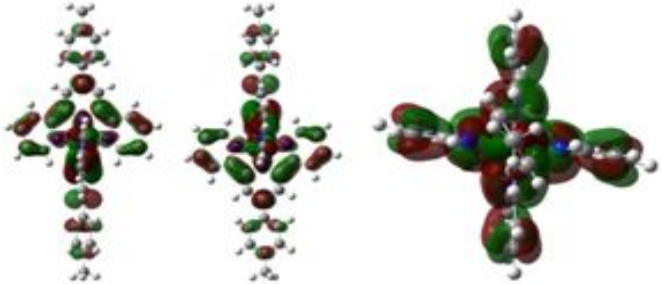
MO 178 (LUMO+1)



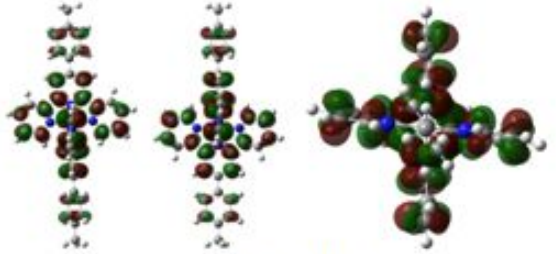
MO 176 (HOMO)



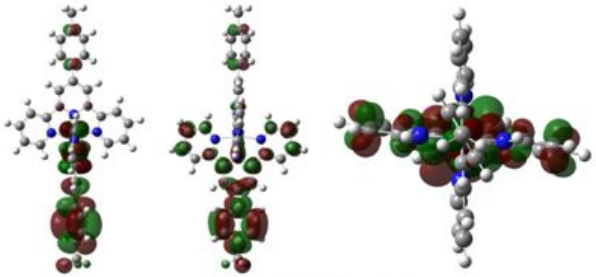
MO 184 (LUMO+7)



MO 177 (LUMO)

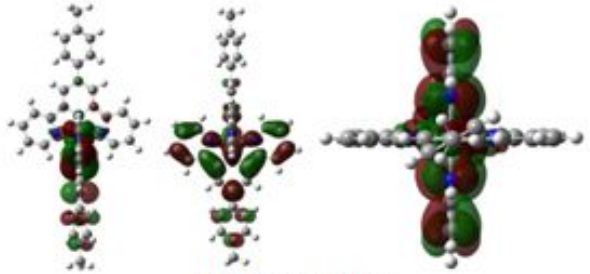


MO 186 (LUMO+9)

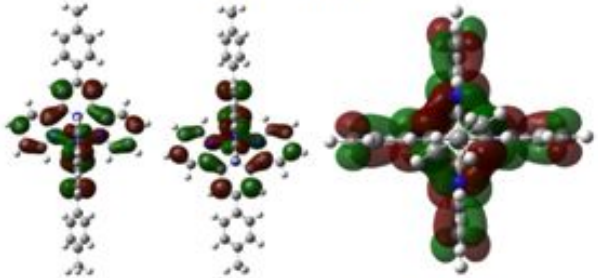


MO 190 (LUMO+13)

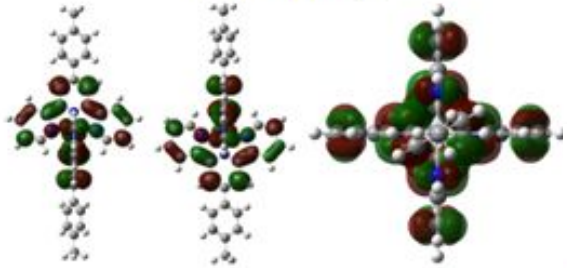
Molecular orbitals involved in intense transitions of the [Si(ttpy)2]+2 structure



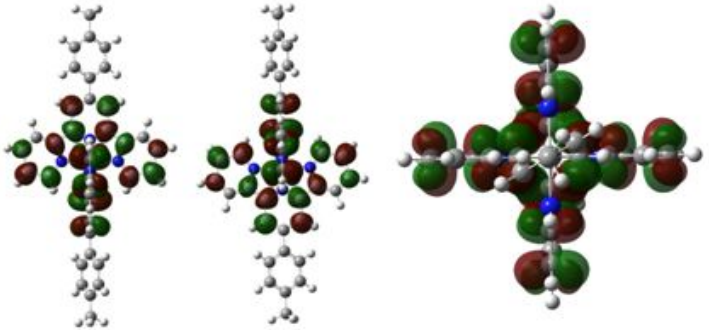
MO 177 (HOMO)



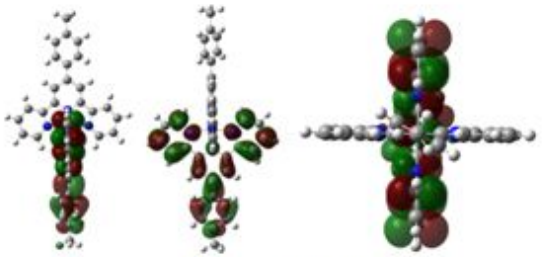
MO 178 (LUMO)



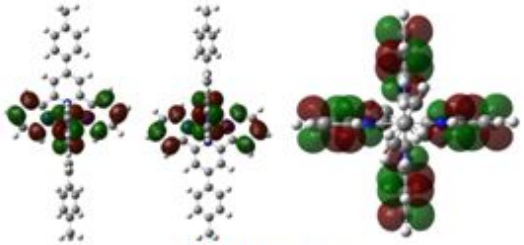
MO 179 (LUMO+1)



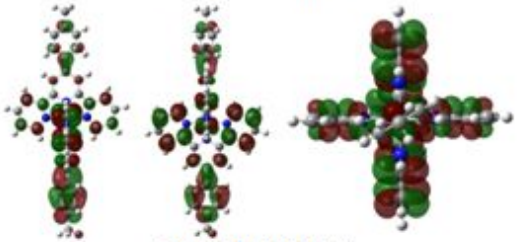
MO 190 (LUMO+12)



MO 181 (LUMO+3)

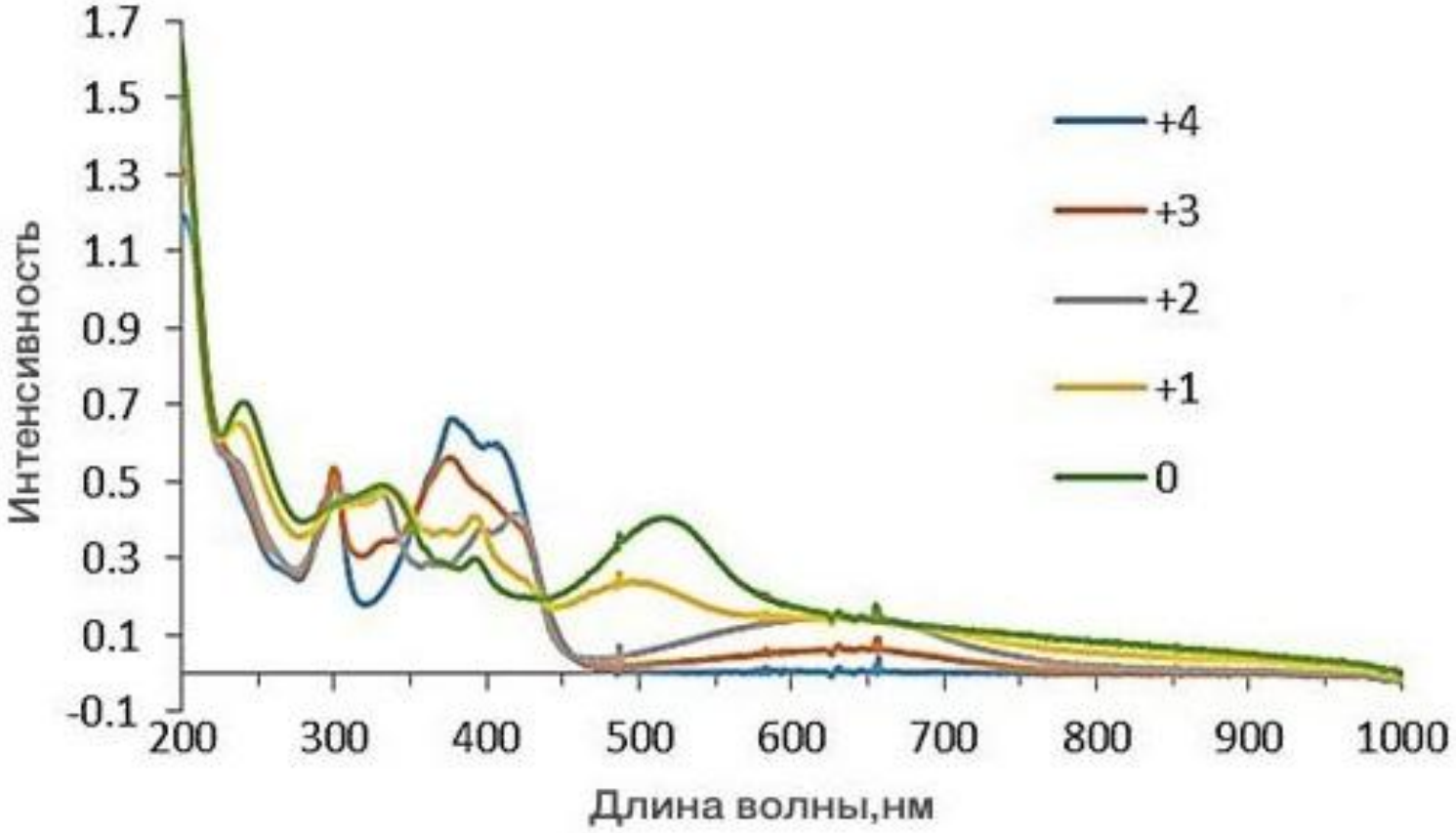


MO 182 (LUMO+4)



MO 185 (LUMO+7)

Molecular orbitals involved in intensive transitions of the [Si(ttpy)2]0 structure



The spectra of the [Si(ttpy)2]+n states are electrochemically generated at -0.245 V (blue line, n = 4), -0.520 V (red line, n = 3), -0.945 V (grey line, n = 2), -1.370 V (yellow line, n = 1), and -1.695 V (green line, n = 0)

Conclusion

- Quantum-chemical calculation of the structural parameters of [Si(pincer)2]0 ; [Si(ttpy)2]+4 ; [Si(ttpy)2] +2 ; [Si(ttpy)2] 0 complexes has been performed by the DFT method and their electro-optical properties have been studied. The results obtained were compared with known experimental data.
- Manipulation with the charge substituents of the Si(ttpy)2 complex can provide the desired electro-optical properties of the material. It is shown how the change in the charge of the complex with ttpy ligand affects the electronic absorption spectrum.
- The probabilities of electronic transitions and the nature of the molecular orbitals involved in them are determined. From the visualized MOs we can say that all of them have the nature of π-orbitals and are localized on pyridine ligands.

Thank you for your attention!