DFT calculation of optical properties of new neutral hexacoordinated Si(bzimpy) 2 complexes

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We consider optical properties of 4 neutral hexacoordinated Si(bzimpy)$_2$ complexes, containing the 2,6-bis(benzimidazol-2'-yl) pyridine ligand using DFT method. The geometrical parameters of the optimized cluster structures, the electronic absorption spectrum, and the molecular orbitals of the structures under consideration are discussed. The effect of addition of the substituents ligands to the of Si(bzimpy)$_2$ compound is considered. We found that succesive addition of substituents shifts HOMO and LUMO to higher values. The manipulation may provide desirable optical properties of the material.

Keywords: DFT, silicon hexacoordinated complexes, electronic absorption spectrum.

Introduction

There has been a sustained interest in developing new materials for organic electronic devices, and there is particularly a need for new low molecular weight, chemically and electrochemically robust, ETL materials. The tetravalent silicon center provides the opportunity to explore a Si(bzimpy)$_2$ design, consisting of two dianionic pincer ligands. This design could provide greater stability, low molecular weights, low dipole moments, and the opportunity to tune redox and optical properties through synthetic design of the pincer ligand Si(ligand)$_2$ complexes are a promising new class of metal chelates for organic electronic devices, and the rich synthetic diversity of dianionic pincer ligands should provide a number of

desirable and tailorable complexes for electron transport and electroluminescence applications [1].

In recent years, there has been a significant increase in the structural diversity of stable hexacoordinate silicon complexes, especially ones containing *N* or *O* chelating ligands, and the bipyridine ligand is an especially well-known and important ligand for stabilizing hexacoordinate silicon complexes [2-7].

In this paper, the object of study are the neutral hexacoordinated Si(bzimpy)$_2$ complexes, containing the 2,6-bis(benzimidazol-2'-yl) pyridine ligand. The purpose of this work is to consider the optical properties, based on the density functional theory, of new neutral hexacoordinated Si(bzimpy)$_2$ complexes.

Calculation methods

All quantum-chemical calculations of the hexacoordinated Si(bzimpy)$_2$ complexes have been carried out using density functional method, implemented in the Gaussian09 software package [8]. Nowadays, this method includes a wide range of different functional. Properties of the objects have been calculated using B3LYP functional [9-11].

«1»   R=H and R'=H

«2»   R=OCH$_3$ and R'=H

«3»   R=H and R'=CH$_3$

«4»   R=OCH$_3$ and R'=CH$_3$
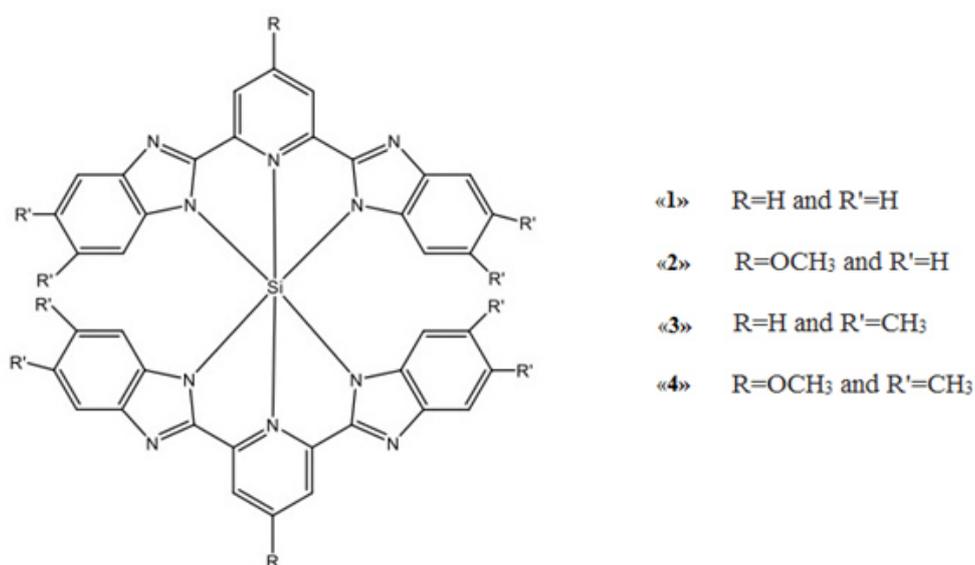
Figure 1. Chemical structure of observed types of hexacoordinate silicon complexes.

All calculations carried out using the computational resources of the National Scientific Laboratory for the shared use of information and Space Technologies at the Kazakh National Research Technical University named after K.I. Satpayev [12].

Structure optimization

For calculations, it was decided to pay attention to the clusters: '1' Si(2,6-bis-benzimidazolyl)$_2$, '2' Si(2,6-bis-benzimidazolyl-4-methoxypyridine)$_2$, '3' Si(2,6-bis-benzimidazolyl-4-methylpyridine)$_2$, '4' Si(2,6-bis-dimethylbenzimidazolyl-4-methoxypyridine)$_2$ (Figure 1). The structures were built according to known

experimental data [13]. Optimization was performed with B3LYP/6-31G* functional and basis set [14-23].

Table 1 presents the geometrical parameters of the optimized cluster structures. Figure 2 shows the final structures after complete optimization of the complexes.

Table 1.
The structural data of the Si(bzimpy)$_2$ complexes.

Compound	2D model	Molecular formula	Bond lengths (Å)		Bond angles (°)	
Si(2,6-bis-benzimidazolyl)$_2$		C$_{38}$H$_{22}$N$_{10}$Si	Si-N^2	1.898	N^2-Si^1-N^{37}	179.999
			Si-N^{12}	1.902	N^2-Si^1-N^{12}	81.754
			N^2-C^3	1.353	N^{12}-Si^1-N^{37}	98.246
			N^9-C^8	1.319	Si^1-N^2-C^3	118.474
			N^{12}-C^8	1.380	Si^1-N^{12}-C^8	114.920
			N^9-C^{10}	1.376	N^2-C^3-C^4	119.710
			N^{12}-C^{11}	1.381	C^3-C^4-C^5	118.052
			C^3-C^4	1.394	C^4-C^5-C^6	121.423
			C^4-C^5	1.398	N^{12}-C^8-N^9	116.599
			C^3-C^8	1.444	C^8-N^9-C^{10}	103.015
			C^{10}-C^{11}	1.431	C^8-N^{12}-C^{11}	103.758
			C^{10}-C^{13}	1.404	N^{12}-C^{11}C^{10}	106.214
			C^{13}-C^{14}	1.385	C^{16}-C^{11}-C^{10}	120.740
			C^{14}-C^{15}	1.413	C^4-C^5-H^{27}	119.289
			C^5-H^{27}	1.086	C^3-C^4-H^{26}	119.453
Si(2,6-bis-benzimidazolyl-4-methoxypyridine)$_2$		C$_{40}$H$_{26}$N$_{10}$O$_2$Si	Si-N^2	1.890	N^2-Si^1-N^{37}	179.635
			Si-N^{12}	1.908	N^2-Si^1-N^{12}	81.633
			N^2-C^3	1.351	N^{12}-Si^1-N^{37}	98.095
			N^9-C^8	1.319	Si^1-N^2-C^3	118.914
			N^{12}-C^8	1.379	Si^1-N^{12}-C^8	114.850
			N^9-C^{10}	1.376	N^2-C^3-C^4	120.728
			N^{12}-C^{11}	1.380	C^3-C^4-C^5	117.866
			C^3-C^4	1.389	C^4-C^5-C^6	120.570
			C^4-C^5	1.408	N^{12}-C^8-N^9	116.689
			C^3-C^8	1.446	C^8-N^9-C^{10}	102.940
			C^{10}-C^{11}	1.431	C^8-N^{12}-C^{11}	103.745
			C^{10}-C^{13}	1.404	N^{12}-C^{11}C^{10}	106.255
			C^{13}-C^{14}	1.385	C^{16}-C^{11}-C^{10}	120.773
			C^{14}-C^{15}	1.413	C^{14}-C^{13}-H^{29}	121.917
			C^{13}-H^{29}	1.085	C^3-C^4-H^{26}	118.784
			C^5-O^{27}	1.342	C^4-C^5-O^{27}	124.027
			O^{27}-C^{72}	1.430	C^5-O^{27}-C^{72}	119.177
			C^{72}-H^{77}	1.090	O^{27}-C^{72}-H^{77}	105.412
					O^{27}-C^{72}-H^{79}	111.020
Si(2,6-bis-benzimidazolyl-4-methylpyridine)$_2$		C$_{46}$H$_{38}$N$_{10}$Si	Si-N^2	1.898	N^2-Si^1-N^{37}	179.997
			Si-N^{12}	1.902	N^2-Si^1-N^{12}	81.751
			N^2-C^3	1.354	N^{12}-Si^1-N^{37}	98.247
			N^9-C^8	1.320	Si^1-N^2-C^3	118.457
			N^{12}-C^8	1.381	Si^1-N^{12}-C^8	114.917
			N^9-C^{10}	1.375	N^2-C^3-C^4	119.669
			N^{12}-C^{11}	1.380	C^3-C^4-C^5	118.057
			C^3-C^4	1.395	C^4-C^5-C^6	121.460
			C^4-C^5	1.398	N^{12}-C^8-N^9	116.488
			C^3-C^8	1.443	C^8-N^9-C^{10}	102.933
			C^{10}-C^{11}	1.426	C^8-N^{12}-C^{11}	103.694
			C^{10}-C^{13}	1.404	N^{12}-C^{11}C^{10}	106.337
			C^{13}-C^{14}	1.387	C^{16}-C^{11}-C^{10}	120.359
			C^{14}-C^{15}	1.432	C^4-C^5-H^{27}	119.270
			C^5-H^{27}	1.086	C^3-C^4-H^{26}	119.441
			C^{14}-C^{30}	1.511	C^{16}-C^{15}-C^{31}	119.271
			C^{15}-C^{31}	1.510	C^{13}-C^{14}-C^{30}	119.854
			C^{30}-H^{73}	1.094	C^{14}-C^{30}-H^{73}	110.842
			C^{31}-H^{77}	1.097	C^{15}-C^{31}-H^{76}	111.800

Continuation of the Table 1.
The structural data of the Si(bzimpy)$_2$ complexes.

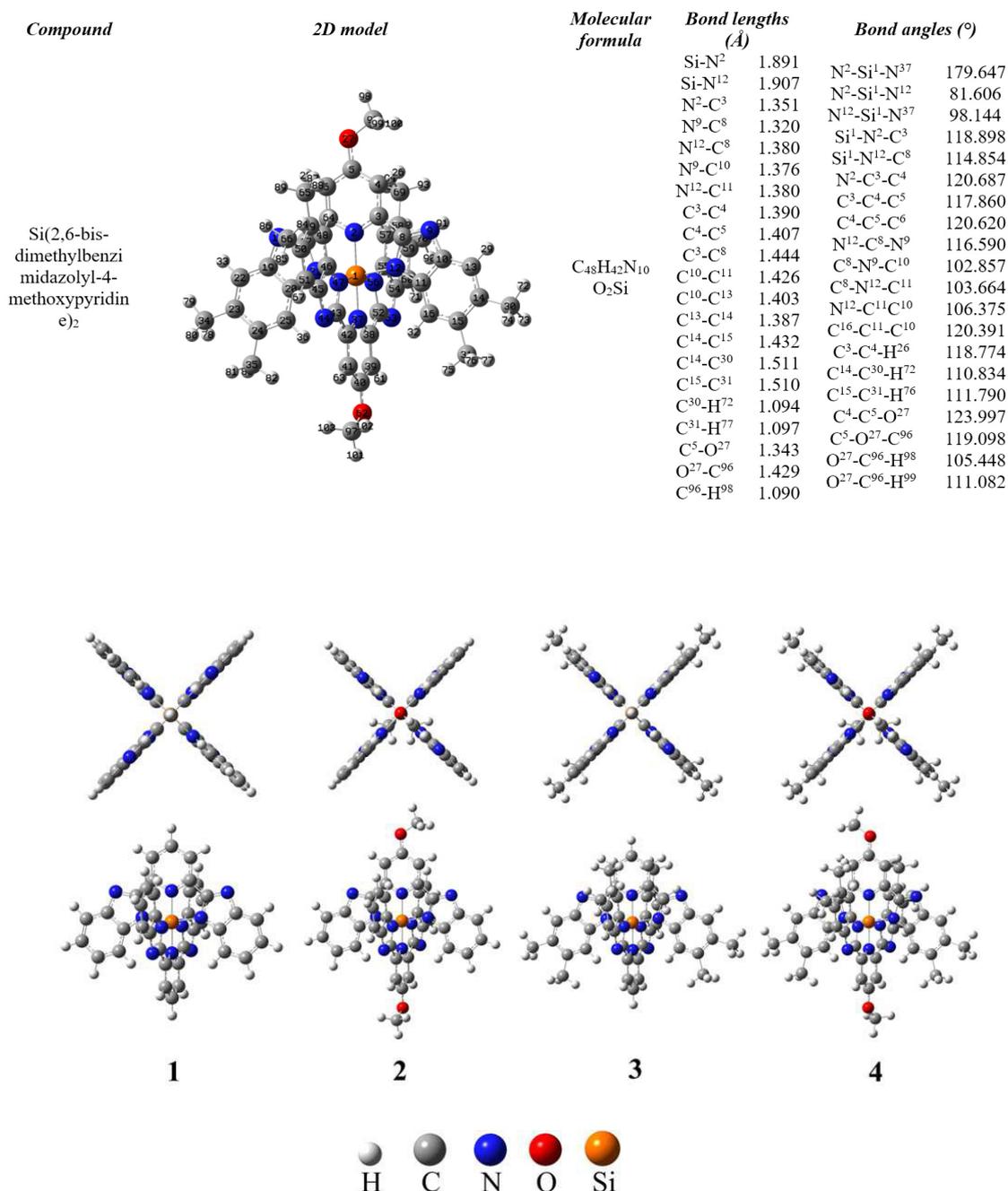| Compound	2D model	Molecular formula	Bond lengths (Å)		Bond angles (°)	
Si(2,6-bis-dimethylbenzi midazolyl-4-methoxypyridin e)$_2$		C$_{48}$H$_{42}$N$_{10}$O$_2$Si	Si-N^2	1.891	N^2-Si^1-N^{37}	179.647
			Si-N^{12}	1.907	N^2-Si^1-N^{12}	81.606
			N^2-C^3	1.351	N^{12}-Si^1-N^{37}	98.144
			N^9-C^8	1.320	Si^1-N^2-C^3	118.898
			N^{12}-C^8	1.380	Si^1-N^{12}-C^8	114.854
			N^9-C^{10}	1.376	N^2-C^3-C^4	120.687
			N^{12}-C^{11}	1.380	C^3-C^4-C^5	117.860
			C^3-C^4	1.390	C^4-C^5-C^6	120.620
			C^4-C^5	1.407	N^{12}-C^8-N^9	116.590
			C^3-C^8	1.444	C^8-N^9-C^{10}	102.857
			C^{10}-C^{11}	1.426	C^8-N^{12}-C^{11}	103.664
			C^{10}-C^{13}	1.403	N^{12}-C^{11}C^{10}	106.375
			C^{13}-C^{14}	1.387	C^{16}-C^{11}-C^{10}	120.391
			C^{14}-C^{15}	1.432	C^3-C^4-H^{26}	118.774
			C^{14}-C^{30}	1.511	C^{14}-C^{30}-H^{72}	110.834
			C^{15}-C^{31}	1.510	C^{15}-C^{31}-H^{76}	111.790
			C^{30}-H^{72}	1.094	C^4-C^5-O^{27}	123.997
			C^{31}-H^{77}	1.097	C^5-O^{27}-C^{96}	119.098
			C^5-O^{27}	1.343	O^{27}-C^{96}-H^{98}	105.448
			O^{27}-C^{96}	1.429	O^{27}-C^{96}-H^{99}	111.082
			C^{96}-H^{98}	1.090		

Figure 2. Optimized structures of nanoparticles.

AB INITIO calculation of the electronic absorption spectrum

The electronic absorption spectrum of the optimized structures was calculated by the time-dependent density functional theory TD DFT [24-30]. Intense transitions of the calculated absorption spectra are presented in Table 2.

Table 2.
Intense transitions of the calculated absorption spectra.

Compound	Transition number	(λ) Wavelength, nm	(f) Oscillator strengths	MO transition
Si(2,6–bis–benzimidazolyl)$_2$	5	437	0.2510	HOMO-2 ->LUMO
	6	437	0.2510	HOMO-2 ->LUMO+1
	23	353	0.1300	HOMO-5 ->LUMO+2
	24	353	0.1300	HOMO-6 ->LUMO+2
Si(2,6–bis–benzimidazolyl–4–methoxy-pyridine)$_2$	5	401	0.1111	HOMO-2 ->LUMO
	6	400	0.1507	HOMO-2 ->LUMO+1
	23	351	0.1008	HOMO-5 ->LUMO+2
	24	350	0.1027	HOMO-6 ->LUMO+2
Si(2,6–bis–benzimidazolyl–4–methoxy-pyridine)$_2$	5	454	0.2167	HOMO-2 ->LUMO
	6	454	0.2167	HOMO-2 ->LUMO+1
	23	367	0.1214	HOMO-5 ->LUMO+2
	24	367	0.1214	HOMO-6 ->LUMO+2
	25	353	0.1205	HOMO-3 ->LUMO+3
	26	353	0.1205	HOMO-4 ->LUMO+3
	28	347	0.1419	HOMO-5 ->LUMO+3
	29	347	0.1418	HOMO-6 ->LUMO+3
	31	340	0.4885	HOMO -> LUMO+3
Si(2,6–bis–dimethyl-benzimidazolyl–4–methoxy-pyridine)$_2$	1	431	0.1037	HOMO -> LUMO
	2	431	0.1036	HOMO -> LUMO+1
	5	415	0.1438	HOMO-2 -> LUMO
	6	414	0.1500	HOMO-2 ->LUMO+1
	25	351	0.1226	HOMO-3 ->LUMO+3
	26	351	0.1378	HOMO-4 ->LUMO+3
	28	345	0.1410	HOMO-5 ->LUMO+3

Figure 3 shows the calculated electronic absorption spectra of silicon complexes (**1, 2, 3, 4**), reconstructed by the GaussView 5.0 software package with a half-width at half-height of 0.3 eV. The most degenerate peaks are observed in the wavelength region 330-350 nm. The initially constructed structure '**1**' has the lowest intensity peak around 330 nm. A further increase of molecule by adding the OCH$_3$ group to the previous structure '**1**' leads to an increase in the absorption intensity in the second structure '**2**'. In the following cluster '**3**', the addition of the CH$_3$ group to the structure '**1**' leads to a shift of the spectrum towards the long-wavelength region. In the last cluster '**4**' obtained by adding the groups CH$_3$ and OCH$_3$ to the structure '**1**', the highest peak in absorption intensity is clearly observed.

For the complexes '**1**' and '**3**' it is noted the appearance of absorption peaks in the long-wave region of the spectrum 435-455 nm, which is absent in the other 2 structures '**2**' and '**4**'. There is a tendency to increase the intensity of absorption with increasing number of atoms in the clusters under consideration.

Figure 4 shows the location of the frontier molecular orbitals levels. HOMO levels with sequential addition of substituents in the range **1, 2, 3, 4** increase in

energy. Levels of LUMO are increased for complexes **'2'** and **'4'**, in the case of **'3'** it is almost the same as for **'1'**. After reviewing the visualized molecular orbitals of clusters of all four types of silicon, it can be said that they all have the nature of the π-orbitals and localized on the pincer ligands (Figure 5).
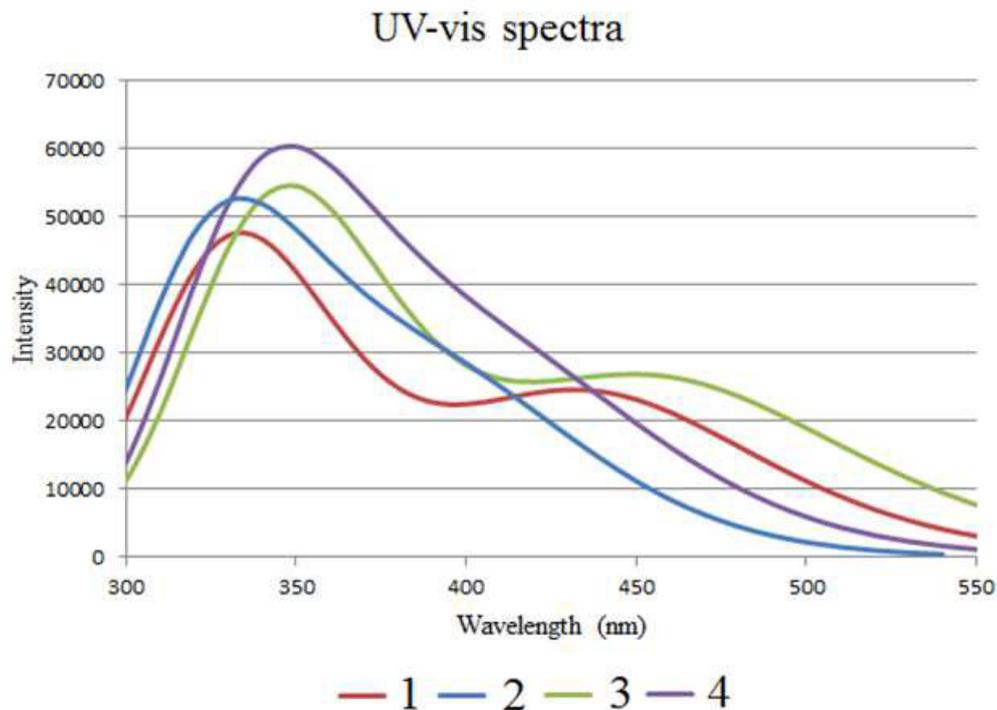

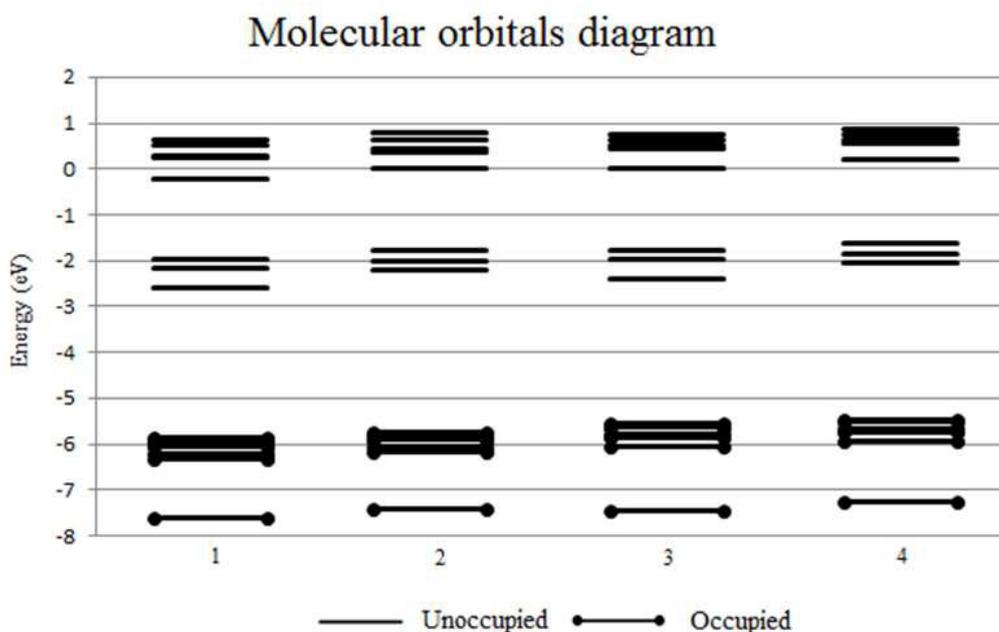Figure 3. Calculated electronic absorption spectra of silicon complexes **1, 2, 3** and **4**.

Figure 4. Diagram of molecular orbitals of the silicon clusters.
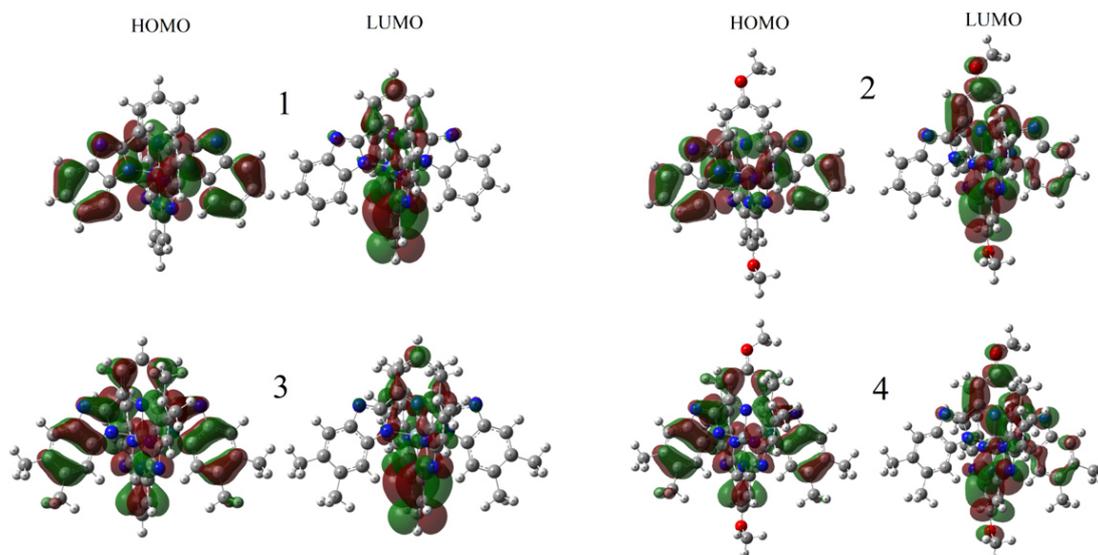
Figure 5. HOMO and LUMO of the complexes **1, 2, 3** and **4**.

Conclusion

Addition of the OCH_3 ligands to the ligands of $Si(bzimpy)_2$ compound leads to decrease of long-wave absorption peak at 430 nm. All intense transitions in electronic spectra of the compounds **1-4** relate to molecular orbitals localized on the bzimpy ligands. A succesive addition of OCH_3, CH_3 and OCH_3 with CH_3 substituents to $Si(bzimpy)_2$ complex shifts HOMO and LUMO to higher values. Thus, the manipulation with substituents of $Si(bzimpy)_2$ complex may provide desirable optical properties of the material.

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