

Structure of poly(di-n-hexylsilane) in nanoporous materials

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ABSTRACT

In this work the effects of solvent polarity and conformation changing on the electronic characteristics of poly(di-n-hexylsilane) incorporated in the nanoporous materials are calculated. The dependence of energy levels of electronic-excited states of investigated compounds is analyzed as a function of the Si–Si–Si–Si twist angle and length of Si–Si and Si–C bonds. The possibility of complex formation between silicon atom of polymer and oxygen ions of nanoporous materials is shown.

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1. Introduction

The optical properties of polysilanes have several applications. In the field of organosilicon chemistry, polysilanes have received worth-while attention of researchers because of their remarkable spectral characteristics [1,2]. Polysilanes are sigma-conjugated high polymers with a Si backbone and carbon-based side groups. This unique structure poses a particular series of challenges in the field of photophysics of compounds with delocalized excited states. Understanding of optical properties of conjugated polymers and in particular the degree of localization of excitations opens wide opportunities for practical application in photochemical and non-linear optic [3].

Among polysilanes, the poly(di-n-hexylsilane) (PDHS) is the most extensively studied polymer. It has been widely investigated in the last decades experimentally and theoretically [4–6]. It is known that at room temperature PDHS is highly crystalline with a trans-planar configuration of segments of a chain (the planar zig-zag conformation) and absorbs in 370–380 nm. In solution, the so-called “rod” form of the polymeric molecule absorbs at much shorter wavelengths (317 nm) than the crystalline phase at room temperature. The spectral shift of the absorption band towards shorter wavelength is the result of changes in polymer conformation [7]. Although questions related to the structure and electronic state have been described in detail, the difference between the

position of UV absorption band for “rod” form in solution and for crystalline form is still unexplored.

On the other hand, the polymeric materials in porous matrices exhibit a series of properties which were not observed in isolated state. Recently it was indicated that the spectral properties of pure PDHS and PDHS embedded in nanoporous silica material are different [8]. Furthermore these properties depend on size of the pores. Such compositions as “host–guest” were used [9,10]. Hence, to interpret the mechanism of polysilane molecules interaction with active sites of walls of pores the experiment was carried out. Photoluminescence spectra of the nanosized PDHS incorporated in the mesoporous materials with pore diameters of 2.8 nm consist of two bands maxima at 350 and 410 nm. In the spectrum of the PDHS incorporated into the matrix with pore diameters from 6 to 10 nm, the band at 410 nm is not observed [8]. The origin of a long-wave band at 410 nm in the fluorescence spectra of PDHS in nanoporous materials with a pore diameter 2.8 nm is unexplored yet. This situation was clarified by computation studies of PDHS–nanoporous materials systems.

In order to elucidate the nature of the experimentally observed spectral changes and to provide information about the polymer conformation towards the matrix, the semi-empirical calculations were used for PDHS. The comparison of experimental and theoretical calculations of electronic structure of PDHS will provide the requisite information for polymeric applications.

2. Computational details

In this work, the calculations of energy parameters of the investigated polymer conformation were performed using the

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TD/CEP-31G method (Gaussian 98). Semi-empirical quantum-chemical calculations were carried out by AM1 method (HyperChem 7.0) with full optimization of the geometry of molecules. The transition energies and the oscillator strengths were calculated with configuration interaction of wave functions, where all electronic states were included, which were generated by singly exciting all electrons in the 10 highest occupied molecular orbital (HOMO) to the 10 lowest unoccupied molecular orbital (LUMO) with respect to the ground state.

In order to examine the conformational changes on the position of absorption band of PDHS spectra, the following parameters of the polymer molecules have been selected from work [7]: the values of bond lengths for Si–Si as 2.355 Å and Si–C as 1.88 Å, respectively. The value of Si–Si–Si angle was taken as the experimentally observed value of 120°, and the C–Si–C angle as 109.34°. The polymer conformational repeat unit was taken to be defined by the rotations about two consecutive Si–Si bonds.

The variation of energy of the lowest singlet levels against the twist angle (φ) was scanned by full optimization of the rest of the geometry at every point. The points were selected at intervals of $\varphi = 5^\circ$ in the range 80°–260°.

The complex was modelled by interaction of trailer silicon atom of the polymer with oxygen atom O^- of surface area (the second valence of oxygen atom for calculation simplification is closed by hydrogen atom as a non-significant influence on spectral characteristics). The connection of any atoms with silicon atom of a skeleton chain is impossible due to steric difficulties. It is possible only to trailer silicon atom.

For theoretical studies of the effect of solvent polarity on energy characteristics of a polymeric molecule, we used polarized continuum method (PCM) [11].

3. Result and discussion

The nature of visible fluorescence of PDHS is discussed in the literature till now, especially during the last decade due to the advancement of both experimental techniques and evolution of molecular modelling and quantum chemical procedure [12–14]. The existing models assume that the visible fluorescence of PDHS can be attributed to the presence in polysilanes as aryl, and alkyl side groups [15,16], and also depends on the length of alkyl substitutes [12,17]. An alternative explanation is that the defects in polymeric chains caused by conformations of polymeric chain are responsible for the fluorescence spectra of PDHS in the visible region [10]. At room temperature, the optical properties of siliceous MCM-41, MCM-48, SBA-15 show strong blue-green photoluminescence. Twofold coordinated silicon centres in the tested samples are responsible for the bands at 440 nm in photoluminescence spectra [18].

The photoluminescence spectra of the nanosized PDHS incorporated in the mesoporous material with 2.8 nm pore diameter are shown in Fig. 1. Curve 2 consists of narrow band with a maximum at 350 nm and broad band in the visible region with a maximum at 410 nm. The excitation spectrum of the PDHS/silica composites with the pore diameters 2.8 nm recording at 350 nm indicate a strong narrow band with a 346 nm maximum and a weak band with a 336 nm maximum while recording at 410 nm the band of excitation spectrum in addition to the 346 nm band have a new strong band with a maximum at 300 nm [10]. The explanation of the changes observed in spectra of the PDHS composite substantially depends on the structure and the possibility of polymer conformation modelling.

We analyzed the changes observed in the optical spectra of the nanostructure PDHS by increasing number of atoms from 2 to 6. We estimated that this changing led to the negligible increases of

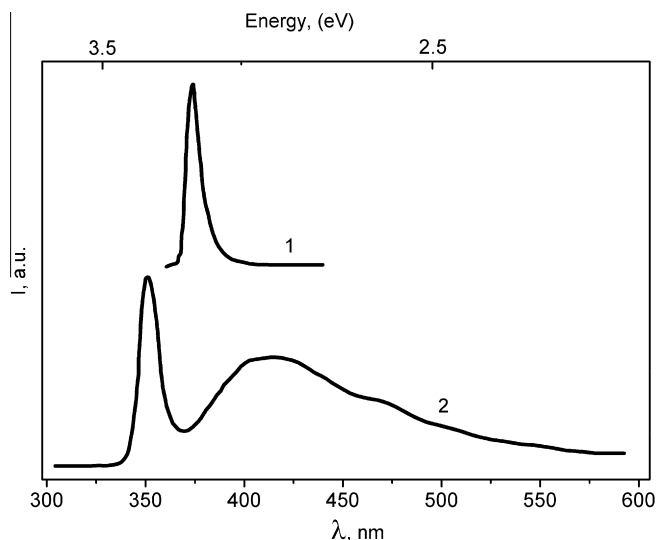


Fig. 1. The fluorescence spectra of PDHS ($T = 5$ K): (1) PDHS/MCM-41 ($dp = 2.8$ nm); (2) thin film [5].

energy of the second and the third singlet levels. The position of the first singlet level was not practically changed even under increasing the number of Si atoms up to 8. Thus, such an increase of the number of atoms of polymer practically did not affect on position of the band of the absorption spectra.

The polymeric model was constructed starting from seven silicon atoms with an angle between the atoms of silicon as 120°. All further structures differed only in the angle of twisting of the polymeric chain. The geometry of other part of polymer did not change significantly.

The energy of the lowest $\sigma \rightarrow \sigma^*$ transitions and the oscillator strength for all conformations were investigated as a function of the twist angle. The variation of the total energy and the lowest singlet levels S_1 and S_2 versus the twist angle for polymeric molecule are graphically shown in Fig. 2(a) and (b), respectively.

The lowest energy conformation for the PDHS at twist angle of the chain at 180° is evident from Fig. 2(a). The step-by-step twisting of Si–Si–Si–Si chain of a polymeric molecule to an angle 140° was accompanied by an increase of the energy of S_1 -level and an increase in oscillator strength of this transition. The energy of S_2 -level and oscillator strength of transition decreased (from $f = 0.59$ to 0.28). It is possible to determine two points on the representative curve with identical energy corresponding to the conformations of the polymer molecules with a twisting angle of 140° and 220° between atoms Si–Si–Si–Si. At these points there is an inversion of energy levels. Thus, the possible changes of molecule conformation resulted in the shift of long-wavelength absorption band by an average of about 12 nm, whereas the experimental value is much more. The low-energy conformation with a twisting angle of about 180° as illustrated in Fig. 2(a) was realized in PDHS/MCM-41 composite.

Different numbers of bond lengths of Si–C and Si–Si were selected in order to assess their dependence onto position of the lowest singlet levels. The analogous dependence was described earlier for heteroaromatic molecules [19,20]. The obtained data are presented in Fig. 3. In the presented graphic any change in Si–Si bond length in comparison with crystallographic data (2.355 Å [7]) has led to energy decrease of the lowest singlet level. This fact explains the shift of the peak in the absorption spectra of films in comparison with the spectra of polymer solutions where changes of length Si–Si bond are not possible.

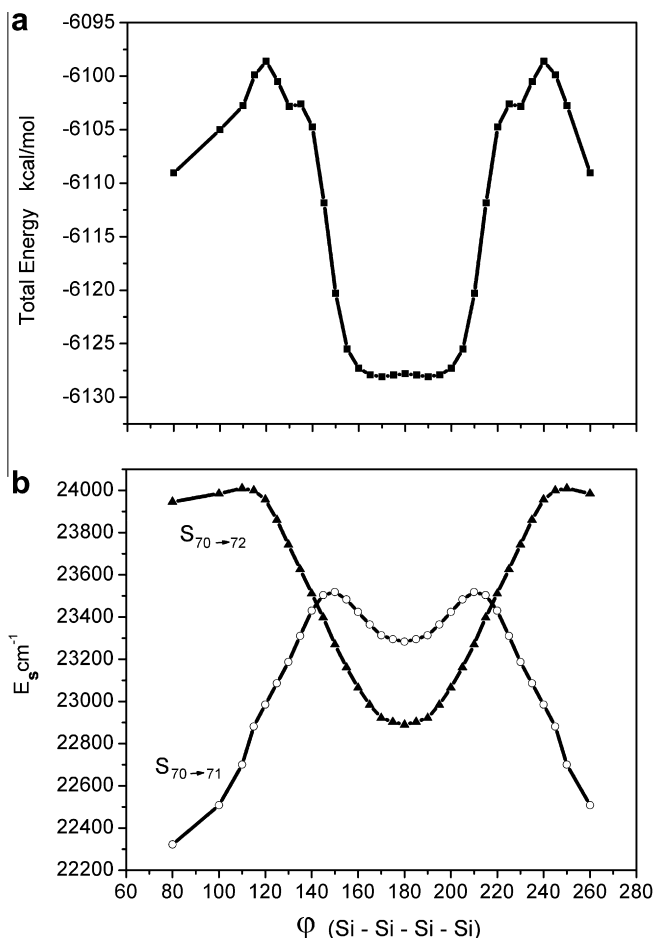


Fig. 2. Plot of total energy (a) and energy of the lowest singlet levels (b) versus the twist angle of polymeric molecule.

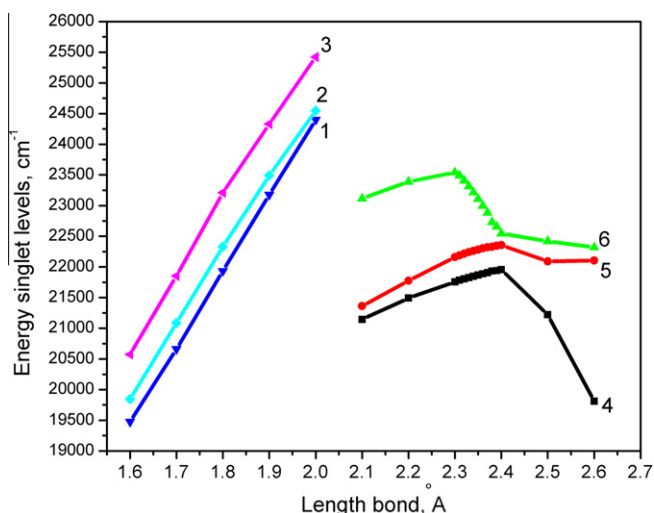


Fig. 3. The dependence of energy of singlet S_1 , S_2 , S_3 -levels on the bond length Si-C (curves 1, 2, 3) and on the bond length Si-Si (curves 4, 5, 6).

Significant changes of energy of singlet levels have been observed at increased Si-C bond length from 1.6 to 2.0 Å: $\Delta S_1 = 4924 \text{ cm}^{-1}$, $\Delta S_2 = 4703 \text{ cm}^{-1}$. Thus, the hypsochromic shift of absorption spectra of polymer films at increase of temperature, which was observed experimentally [21], can be correlated to the increasing of the Si-C bond length above 1.88 Å.

The influence of solvent polarity on the electronic characteristics of PDHS was discussed on the basis of results of calculations and experiments. The PDHS polymer was incorporated into the porous matrix from the 1 wt.% solution in toluene. In the work [10] it was mentioned that during preparation of such composite material the polymer solution was poured in the nanoporous silica. Thus if the incorporated agent was placed inside of the pore by using solvents, the hypothesis of solvent presence in the pores of silica cannot be excluded. Hence in this work we also assessed the effect of solvent presence on the incorporated poly(di-n-hexylsilane) in nanoporous materials.

From positions of absorption spectra of the studied compounds (λ_{max}) and Kirkwood–Onzager constants ($K = \frac{\epsilon-1}{2\epsilon+1}$), a correlation is investigated for an establishment of a degree of solvent effect. The solvents with the values of Kirkwood–Onzager constants from 0.19 (heptane) to 0.49 (water) were used. Only three of the first electron-excited states of molecule were considered.

ΔE (a difference of the lowest singlet levels – S_1 , S_2 , S_3 – of the molecule in solvent and in isolated state) as function of Kirkwood–Onzager constant was plotted on the basis of the calculated values as represented in Fig. 4. It is shown that the energy of S_2 , S_3 -levels for molecules in solvent has a hypsochromic shift in comparison with the energy levels of the isolated molecule. Benzene, toluene, chloroform, acetone, acetonitrile, and DMSO were used as solvents. The position of an S_1 -level remains practically constant and the intensity of this band is very weak ($f = 0.002$) when the value of oscillator strength is considered. The effect of solvent polarity on spectral-luminescent properties of polymer was estimated by the position of second band with the oscillator strength of 0.14. The increase of solvent polarity from less polar benzene ($K = 0.227$) to highly polar DMSO ($K = 0.48$) is the reason for the hypsochromic shift of the S_2 -absorption band: $\Delta E_{S_2} = 0.003 \text{ eV}$, although $\Delta E_{S_1} = 0.0008 \text{ eV}$.

Small changes in the position of maximum absorbance for the spectrum obtained are in good agreement with the experimental data reported by authors: the position of maximum in long-wave absorption band for hexane is 317–318 nm [1], for toluene is 318 nm [22], and for tetrahydrofuran is 318 nm, as well [23]. Changing occurred within the limits of 1 nm and is less than limit of measurement error of absorbance spectra.

Thus, a changing in solvent polarity is not a reason for the appearance of a long-wavelength band in the spectrum of PDHS into a pore MCM-41 with the diameter of 2.8 nm.

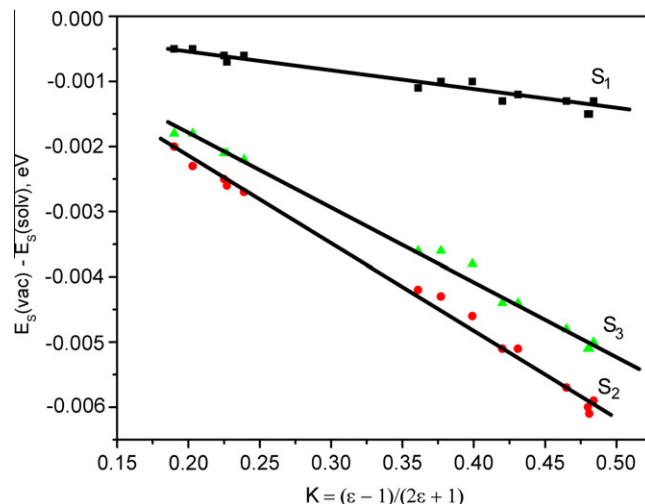


Fig. 4. Plot of ΔE singlet (S_1 , S_2 , S_3) levels of polymer molecules versus Kirkwood–Onzager constant.

The changes in polymer structure incorporated into nanoporous materials were reported in [8,10]. The authors explained it by the processes of interaction of polymer with the surface of the mesoporous material, in which a part of the polymeric chain far from a surface resulted in the appearance of a narrow $\sigma \rightarrow \sigma^*$ band, and defect part resulting in a broad band ($\lambda = 410$ nm) in the PL spectra.

It is reported that the origin of visible fluorescence band in the spectrum of polymer with 2.8 nm size of pores should be due to the changes in polymer conformation [8]. As a result of polymer interaction with the material surface, there is an orientation of polymeric chain along the walls of the pore and, as consequence, can essentially change molecular conformation by changing the angle between Si–Si bonds. A significant change of the local polymer conformation occurs only if the polymer is located in a straight-line orientation with the pore, having Si–OH groups on its surface [21].

By changing conformation the explanation of appearance of long-wavelength fluorescence band of the polymer insight 2.8 nm pore diameter is extremely difficult. Therefore, we have analyzed the possibility of complexes formation between trailer silicon atoms of a polymeric molecule and surface of the pore.

The calculations show that the investigated polymer PDHS does not contain the charged groups, besides, significant positive charge localized on silicon atoms. In our case, apparently, it is necessary to consider a possibility of complex formation between trailer Si atoms of polymer chain and an oxygen ion of walls of the pore: $-\text{Si} \dots \text{O}^- - \text{Al}(\text{Si})$. It is well known that the polysilanes contain the oxygen adsorbed from air, which is an electron acceptor and at atmospheric pressure it can form charge transfer complexes with molecules of many organic compounds. The complexes are rather unstable and easily dissociate at removal of oxygen [24]. The results of the calculation indicate that the cause of complex formation is a significant decrease of the energy of the lowest singlet level, $\Delta E = 3957 \text{ cm}^{-1}$. It leads to conclusion that the formation of such a complex between polymer and walls of a matrix occurs only when the pore diameter is 2.8 nm. Only under these conditions the polymer approaches to the walls of pore as much as it is possible.

The calculated size of separate segment of the PDHS macromolecule is about 1.6 nm. Therefore, only one polymer chain fits into a pore, which has a size 2.8 nm. In this case the incorporated polymer Si–Si–Si–Si chains are isolated from each other; their chains do not interact. The present calculations investigate the total energy variation of electronic state of the complex nanostructured polymer with an oxygen ion of silica MCM-41 at different distances to the walls. Si–O bond distance ranges were from 2 to 10 Å. The plot of total energy versus Si–O bond distance is presented in Fig. 5.

It is noted that the total energy decreases towards minimum value, where the Si–O distance corresponds to the ~ 2.25 Å. At this point we compared the energy of the complex with the energy of the complex components ($E_{\text{complex}} < E_1 + E_2$). The energy of the complex is the largest on 0.393 eV. Thus, when the distance between the components of the complex decreases we observed the decreasing of total energy of system that suggests complex formation.

It is well known that the complex formation is accompanied by the appearance of a long-wavelength band as observed experimentally. The absorption spectrum of poly(di-n-hexylsilanes) incorporated into the MCM-41 pores consists of a strong band with $\lambda_{\text{max}} = 300$ nm and weak band $\lambda_{\text{max}} = 344$ nm as shown by the experimental data [8]. The calculation predicts for a prospective complex the existence of an intensive band with oscillator strength of transition 0.22 and other band with oscillator strength of long-wave transition much less 0.04 corresponding to the experimental data.

According to the calculations the absorption band in long-wavelength region of PDHS spectrum is related to the transitions

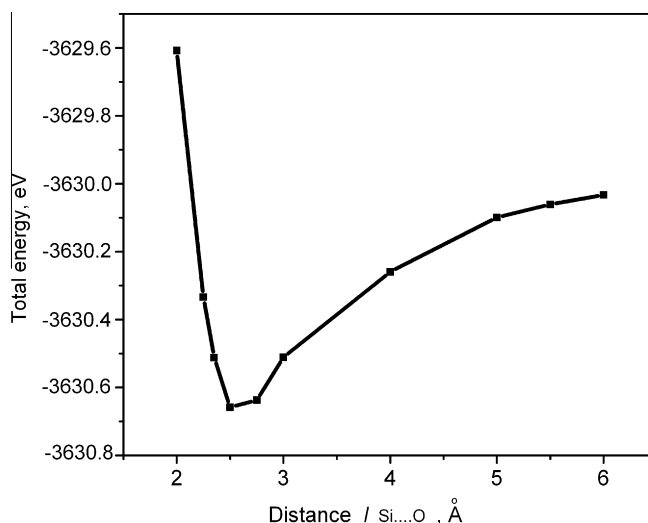


Fig. 5. Plot of total energy values of a complex versus the distances to walls of pore.

between the highest occupied molecular orbital (HOMO) (74) and the lowest unoccupied molecular orbital (LUMO) (75), (78), (79). Its structural data are shown in Table 1.

Thus, for explaining the calculation and the experimental results it is sufficient to analyze the σ -MO structure of the main electronic configurations. As a result of the analysis, we consider that the highest occupied MO (74) was dominantly localized on the oxygen atom of a complex (large $d_\beta(p_i)$ values only on oxygen atom of a complex and not so small on the nearest silicon atom). The MOs of σ -type are four-component and involve linear combinations of s-AO, p_x -AO, p_y -AO and p_z -AO with the coefficients $d_\beta(s)$, $d_\beta(p_x)$, $d_\beta(p_y)$ and $d_\beta(p_z)$, respectively, where β is the nuclear index, with total population of 1. The population is $\rho_i \equiv \sum_\beta [d_\beta(p_i)]^2$, where $i = s, x, y, z$. The value of the population ρ_i of the AO may be of interest in analyzing the localized character of 74-MOs. The population of components (ρ_i) of an oxygen fragment 74 MO is: $\rho_s = 0.000$, $\rho_x = 0.076$, $\rho_y = 0.192$, $\rho_z = 0.556$ and can serve as a generalized feature of such an MO. On the contrary, the value of the population of silicon AO is much smaller: $\rho_s = 0.012$, $\rho_x = 0.000$, $\rho_y = 0.063$, $\rho_z = 0.000$. Thus, the electronic density on 74 (HOMO) orbital is 82% localized over oxygen atom, and on 7.5% over the third atom of silicon of a polymeric chain.

The calculations for 75, 78, 79 and the lowest unoccupied molecular orbital were carried and reported in Table 1. As well as it was supposed, the electronic density on 75 MO is 53.0% localized over the sixth and the seventh silicon atoms and on 37.5% over carbon atom of hexyl radical located near the seventh silicon atom. The electronic density on 78 MO is 90.7% localized over the fourth and the fifth silicon atoms. The electronic density on 79 MO is 92.2% is localized over the third and the fourth silicon atoms. Thus, all the electronic transitions are related to the transfer of electron density from an oxygen ion of a complex to the most remote silicon atom of polymer and to carbon atom of hexyl radical, as a result of which, new absorption band in the UV-vis spectrum can be observed. This absorption is called intramolecular electron transfer or charge transfer.

Thus, from the calculations, it was revealed that in molecular system of a complex the lowest singlet electronic-excited state is formed at the expense of electronic configurations of an oxygen fragment as a result of transition with charge transfer to silicon atoms of a polymeric fragment. This approach is also based on the significant value of Stokes shift suggesting the existence of a band with charge transfer attributed to the radiating complex. We assume that the band with the maximum at 410 nm in the

Table 1

The structural data of HOMO (74) and LUMO (75), (78), (79) of the lowest electronic-excited states of PDHS complex.

	Ψ_{74}				Ψ_{75}				Ψ_{78}				Ψ_{79}			
	$d_{\beta}(s)$	$d_{\beta}(p_x)$	$d_{\beta}(p_y)$	$d_{\beta}(p_z)$	$d_{\beta}(s)$	$d_{\beta}(p_x)$	$d_{\beta}(p_y)$	$d_{\beta}(p_z)$	$d_{\beta}(s)$	$d_{\beta}(p_x)$	$d_{\beta}(p_y)$	$d_{\beta}(p_z)$	$d_{\beta}(s)$	$d_{\beta}(p_x)$	$d_{\beta}(p_y)$	$d_{\beta}(p_z)$
O	0.015	−0.276	−0.438	0.746	−0.000	−0.001	−0.001	0.001	0.007	0.008	0.017	−0.020	−0.007	−0.013	−0.017	0.020
Si ₁	−0.031	−0.022	0.020	0.022	−0.000	−0.000	0.000	−0.000	0.006	0.007	−0.002	0.001	−0.016	−0.011	−0.001	0.004
Si ₂	0.046	−0.010	0.094	0.020	−0.002	0.000	−0.002	0.000	0.041	0.001	0.066	−0.001	−0.048	0.008	−0.073	0.001
Si ₃	−0.112	0.001	0.250	0.000	−0.012	0.021	−0.007	0.000	0.051	−0.061	−0.001	−0.000	−0.255	0.615	−0.226	0.000
Si ₄	0.004	0.010	0.002	0.001	−0.023	0.008	−0.045	0.000	0.253	−0.055	0.659	0.000	0.306	0.578	−0.056	0.000
Si ₅	−0.017	0.000	0.031	0.000	−0.085	0.181	−0.090	0.000	−0.316	0.164	0.531	0.000	0.020	−0.072	0.126	0.000
Si ₆	0.003	0.007	−0.002	0.000	−0.069	0.133	−0.311	0.000	−0.012	0.121	−0.136	0.000	−0.034	−0.059	−0.021	0.000
Si ₇	−0.002	0.000	0.005	0.000	−0.121	0.485	−0.409	0.000	0.049	−0.052	−0.061	0.000	0.003	−0.004	−0.023	0.000
C	0.001	0.001	−0.000	0.000	0.269	0.519	−0.195	0.000	−0.013	−0.037	0.009	0.000	−0.001	−0.003	−0.010	0.000

PL spectrum of PDHS incorporated into the 2.8 nm pores is due to the formation of such a complex.

4. Conclusions

The present quantum-chemical calculations on PDHS provide the theoretical frame work through which the following conclusions can be obtained

- (1) The main structural factor that controls the energy characteristics of an investigating polymer is the twist angle of a polymeric chain, but it cannot explain the experimental results.
- (2) The study shows that the change in Si–Si bond length leads to shifting of the maximum of absorption spectrum upon transition from polymeric films to solutions which does not correspond to the experimental data. However, the shift of the maximum of absorption spectrum can be explained by changing the Si–C bond lengths. The solvent polarity does not influence essentially the absorption spectrum of polymer which is in agreement with the literature data.
- (3) However, the insertion of polymer in nanoporous structure ($d = 2.8$ nm) appreciably changes the position and character of fluorescence spectrum of the investigated compound. It is possible to conclude that such changes occur due to the complex formation between polymer and pore wall of the material.

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