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**by Jan Andzelm, Adam Rawlett, Joshua Orlicki, James Snyder,
and Kim Baldrige**

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14. ABSTRACT The use of optically transparent materials to modulate or impede laser light in a real-time setting is significant. This goal stimulates an interest in metalloporphyrins, phthalocyanines (PCs), naphthalocyanines, and their derivatives. The most desired derivatives would be optically transparent, absorb laser light, and also be soluble in water. PCs, with their stable, planar square structure and highly delocalized π-electron system, are being used in numerous technological applications, such as pigments, in chemical sensors, and more recently, as photosensitizers for photodynamic therapy. The nonlinear optical properties (NLO) of these compounds are of particular importance. Using quantum chemistry methods, we study both visual and NLO properties of phthalocyanines complexes with Si as a central atom. The effect of hydrophilic axial substituents of the material on their optical properties is examined. We are mainly interested in the PEG poly(ethylene oxide) as an axial substituent because it is used in our laboratory to synthesize soluble PC complexes.					
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1. Introduction

Phthalocyanines (PCs) and their derivatives, being important dyes and pigments due to their intense blue or green color, have been studied extensively since the beginning of the previous century. In recent years, PCs have also been used in photocopiers and printers, photovoltaic cells, gas sensors, nonlinear optical modulating devices, photodynamic therapy agents, and many other applications (Kadish et al., 2003). The PCs display interesting properties such as high thermal and chemical stability, efficient light absorption in the red, and semiconducting and photoconducting abilities. These properties result from PCs having a stable macrocyclic, conjugated network of π -electrons leading to high electrical polarizability and rapid, nonlinear response of the charge density to the applied intense electromagnetic fields. The large nonlinear absorption in the visible spectrum together with the ultrafast response time and easy processability (McKeown, 1998) make PCs a very promising modulator of laser beams. Such a device can permit the transmission of the light in the visible region, but also strongly reducing high-intensity laser light. As such the optical modulation properties of PCs are of key importance for many applications.

Optical modulation with PCs was first reported in 1989 for chloroaluminumphthalocyanine (Coulter et al., 1989) and since then many other PCs with these properties have been identified (Torre et al., 2004) mainly due to the versatility of PCs synthetic organic chemistry. The new PC structures can be made by changing the chemistry and conformations of peripheral and axial substituents as well as by varying coordinating central atoms and attaching PC rings to oligomeric or polymeric species (Torre et al., 2004; Perry, 1997; Kadish et al., 2003). The aromatic π -electron system of the PC can be expanded resulting in, for example naphthalocyanines (NCs) that also exhibit superior optical modulation properties (Torre et al., 2004).

The optical modulation properties of PCs can be explained by the so-called reverse saturable absorption (RSA) mechanism. RSA is essentially a sequential two-photon absorption leading to population of excited triplet states of a material by way of first reaching the excited singlet state. The optimal RSA material would have an excited triplet-triplet cross section much larger than the cross section of the ground to first excited singlet-singlet transitions. It is also necessary that the intersystem crossing from the lowest singlet excited state to the lowest triplet excited state be allowed and that the excited state have a long lifetime (Perry, 1997). A practical optical device would also require high concentration of soluble RSA material in the optical beam. This in turn necessitates use of PCs with axial substituents since the free PCs have a tendency to stack due to the strong intermolecular interactions between the planar PCs rings. Stacking of PCs in water significantly affect the optical spectra and degrades their optical modulating capabilities. Various axial substituents have been used to minimize the inter-molecular stacking of PCs in water (Ngai et al., 2001; Shirk et al., 2000).

In this report, we investigate optical absorption as a function of axial substituents in PCs with Si as the central atom (SiPC). We consider hydrophilic substituents such as poly(ethylene oxide) (PEG) oligomers as they lead to a material soluble in water. Both visible absorption (UV-vis) and non-linear (RSA) are studied using quantum chemistry methods.

We use the time dependent density functional theory (TDDFT) (Gross et al., 1996) to probe the excited state properties. This method has been previously shown to provide reasonable predictions for phthalocyanines and metallo-phthalocyanines structures and UV-vis absorption (Ricciardi et al., 2001; Liao et al., 2004, 2005; Wu et al., 2004; Zhang et al., 2005; Gunaratne et al., 2005). Numerous theoretical studies have also been performed for porphyrin complexes (Baerends et al., 2002; Rogers et al., 2003).

The two main excitations peaks of porphyrins, the Q band in visible range and the B (or Soret) band in the UV region has been explained by the “four-orbital model” introduced in 1963 by Gouterman (Gouterman et al., 1963). According to this model, the Q band originates from electron excitations out of the highest occupied molecular orbital (HOMO) and into the lowest unoccupied molecular orbital (LUMO) and LUMO+1, while the B band is due to transitions from HOMO-1 to LUMO and LUMO+1. Later studies have proposed a more detailed explanation involving more than “four orbitals” because the quasi-degeneracy of orbitals close to the HOMO is removed (Toyota et al., 1997). In the case of metallo-phthalocyanines, transition metal orbitals are also involved in the excited states (Edwards and Gouterman, 1970).

We are not aware of any published theoretical investigation for non-linear RSA properties of phthalocyanines. Unlike study of UV-vis spectra which requires calculation of singlet-singlet excitations (S-S), prediction of RSA requires calculation of triplet-triplet (T-T) absorption and ultimately excited singlet-triplet cross-section. A few investigations have been done on excited triplet states for porphyrin derivatives and zinc-porphyrin (Nguyen et al., 2000) as well as meso-diaryloctaalkyl porphyrins (Kyrychenko et al., 2002).

2. Computational Methods

The conformational analyses of the molecular systems described in this study, including structural and orbital arrangements as well as property calculations, were carried out using a variety of computational techniques for comparative purposes, using GAMESS (Schmidt et al., 1993), GAUSSIAN03 (Frisch et al., 2004) and DMol (Delley, 2000). Choice of optimal methodology was made by performing computations on the lead target compound, using B3LYP, PBE, LDA, and PW91 functionals in combination with a variety of basis sets including 6-31G(nd,mp) and 6-311G(nd,mp) [$n = 1, 2$; $m = 0, 1$]. Molecular structures were optimized using the DMol program, with the double numerical basis (DNP) set at the PBE Hamiltonian level (Perdew et al., 1996). We used the delocalized internal algorithm for geometry

optimization. Although this is a highly efficient algorithm it can only find a local minimum close to the initial structure.

Therefore in order to explore the larger configurational space of the rather flexible PEG oligomers attached to PC, we have used molecular dynamics (MD) technique to generate realistic, initial structures for density functional theory (DFT) geometry optimization. The initial structures of compounds with PEG in water were obtained from MD simulations of the molecules immersed in water, represented by a unit cell of 500 water molecules. The structures of SiPC were kept frozen at their DFT-optimized geometries while PEG conformation and water were subjected to heating the system to 900 K for 50 ps followed by annealing in steps of 5 ps/50 K and finally equilibration at 300 K. Discover program with the COMPASS forcefield and the NVT Berendsen thermostat was used. The annealing procedure was found necessary to allow for proper distribution of water molecules in the unit cell. After 100 ps of equilibration the snapshots from such simulations were taken and, after further DFT geometry optimization, used in calculations of excited states. We have identified several conformers within the energy range of 4 kcal/mol. The lowest and the highest energy conformers were used in subsequent calculations. We have also retained some water molecules within the van der Waals radius of the PC structure. This approach allows us to generate various possible structures of the PEG polymer attached to the Si atom of PC. The optimized structures are available as supplementary material.

The UV-Vis spectrum was identified from singlet excitations, while the RSA spectrum was found from the triplet-triplet transitions using the TDDFT methodology. The local density approximation (LDA) and generalized gradient approximation (GGA) calculations can be efficiently performed by using density fitting thus replacing formally N^4 integral algorithm with the more efficient N^3 method. We found that the electronic transitions did not depend significantly on the particular DFT functional approximation and the B3LYP method was therefore used in the majority of our calculations. We have also used the configuration interaction method with single excitations (CIS) within the semiempirical ZINDO/INDO2 approach.

3. Results

A level of methodology, which will be chemically meaningful to guide experiment and push forward our understanding of these systems, was determined by evaluating structural and property invariance with increasing sophistication of basis set and treatment of dynamic electron correlation. Thus sensitivity of results to the choice of quantum chemistry model will be discussed first. Next, results for the PC with the PEG attached will be presented and compared with the recent experimental findings (Huang et al., 2004). The effect of stacking PC rings is then explored in section 3.2.

3.1 Tests of Quantum Model

Attaching two PEG units with a mass of 75 to the SiPC framework allows us to test the performance of various DFT functionals on structural and property predictions. The structure of SiPC-PEG₇₅ (figure 1) was optimized in the gas phase, followed by UV-Vis and RSA property analysis, as described in section 2. Table 1 shows the main excitation energies (in nm) and oscillator strengths (f) calculated at the following levels of theory: B3LYP/631G*, B3LYP/6311G*, LDA/631G*, PW91/631G*, PBE/631G*, and PBE/6311G*, also including results for the ZINDO/INDO2 approximation.

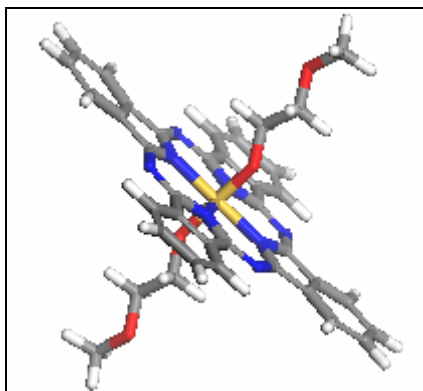


Figure 1. Structure of SiPC-PEG₇₅.

Table 1. Main excitation energies (in nm) and oscillator strengths (f) from UV-Vis (Q and B bands) and RSA (R) calculations of the SiPC-PEG₇₅ model complex.

Method/Excited State	Q	B	R
DFT			
B3LYP/631G*	613 (0.37)	335 (0.54)	479 (0.31)
B3LYP/6311G*	618 (0.38)	338 (0.61)	487 (0.30)
LDA/631G*	624 (0.26)	368 (0.21)	585 (0.41)
PW91/631G*	626 (0.27)	371 (0.20)	578 (0.39)
PBE/631G*	625 (0.27)	371 (0.24)	579 (0.30)
PBE/6311G*	628 (0.28)	362 (0.23)	582 (0.41)
ZINDO/INDO2			
ZINDO(5)//DFT	671 (0.78)	313 (2.40)	—
ZINDO(10)//DFT	671 (0.78)	317 (2.07)	—
ZINDO(20)//DFT	698 (0.77)	337 (1.33)	—
ZINDO(30)//DFT	705 (0.74)	340 (1.27)	—
ZINDO(40)//DFT	717 (0.69)	343 (1.28)	—
ZINDO(50)//DFT	728 (0.66)	349 (1.23)	—
ZINDO(10)//PM3	658 (0.72)	354 (1.07)	—
ZINDO(10)//AM1	643 (0.68)	367 (0.99)	—

The size of the ZINDO CIS expansion is given in parentheses in table 1. In addition to structural results performed at the PBE/DNP level of theory, ZINDO calculations were also performed using semiempirical PM3 and AM1 optimized structure of the complex. The excitations with the largest value of oscillator strength (f) from Q and B bands are presented together with the main RSA transition (R). Currently, the ZINDO program does not have the capability to calculate RSA spectra. The excitation energies of local and gradient-corrected DFT approach appear to be red shifted in comparison to the adiabatic, B3LYP method. The R band, in particular is red shifted by about 60–00 nm. Effects of basis set extension, including diffuse functionality is not significant with a shift in the spectrum by about 10 nm with the more extensive basis set. We have found the density fitting algorithm to be computationally much more efficient while not compromising the quality of the results for electronic spectra. Therefore results obtained at the LDA and GGA level of DFT approximation were performed using the standard density fitting algorithm as implemented in the GAUSSIAN03 program.

The character of transitions was studied (see table 2) and it was found to follow approximately Gouterman's assignments. The Q band is mainly due to the HOMO(H) to LUMO (L) and L+1 excitations. The B band excitations can be interpreted as excitations from several levels below H to L and L+1 levels. The B band appears to be more sensitive to the level of DFT approximation than the B band. The PBE-originated Q band is broader and at the maximum corresponds to transitions to higher virtual orbitals than in the case of the hybrid B3LYP functional (see table 2). The RSA spectra differ significantly depending on selection of the DFT functional. The B3LYP band is broad and covers the entire green part of the spectrum, while the PBE RSA band is very narrow and shifted to the red. The character of the transition is also different with alpha electrons (from the spin-polarized calculations) participating in the spectra for the B3LYP, while the beta electrons dominate the PBE transitions.

Both the local PBE functional as well as the B3LYP hybrid functional approaches predict the absorption of the red light and hence a complementary, green color of the complex. The B3LYP method shows the strong RSA absorption in the expected green region, while the GGA-type method shows triplet-triplet transitions only in the orange part of the spectrum. Based on these results we use the PBE method to determine the color of the complex, while the B3LYP method is used to determine the RSA properties of the system. As such the determination of the UV-Vis spectra can be done with a computationally much more efficient, PBE, method.

The semiempirical ZINDO method offers extremely fast calculations of UV-Vis spectra. Both the Q and B band become red shifted with an increase in the CIS ZINDO expansion. The AM1- and PM3-optimized structures differ significantly from the DFT structure and therefore are not recommended for study of PC complexes. The ZINDO/INDO2 parameters at the DFT geometry, however, reproduces exceptionally well the experimental data (Huang et al., 2004) at low values of CIS expansion, thus making it an attractive method for fast evaluation of the UV-Vis spectra.

Table 2. Character of transitions for major excitation energies (ΔE in nm) and oscillator strengths (f) from B3LYP and PBE calculations with 6311G* basis for SiPC-PEG₇₅ model complex. All electronic states belong to ¹A irrep.

ΔE	Strength (f)	Transition	Weight
B3LYP			
Singlet→Singlet			
618	0.375	H→L	0.603
605	0.371	H→L+1	0.606
339	0.092	H-6→L	0.595
338	0.609	H-6→L	0.577
337	0.524	H-6→L+1	0.489
321	0.120	H→L+5	0.509
320	0.270	H-14→L+1	0.501
Triplet→Triplet			
622	0.141	H-1→L(A)	0.586
528	0.241	H-8→L(B)	0.882
516	0.115	H→L+6(A)	0.696
487	0.300	H-9→L(B)	0.514
483	0.113	H-13→L(B)	0.740
PBE			
Singlet→Singlet			
648	0.195	H→L	0.483
628	0.284	H→L+1	0.578
615	0.093	H-3→L	0.616
404	0.119	H-13→L	0.495
372	0.122	H-17→L+1	0.383
371	0.119	H-17→L+1	0.471
363	0.141	H→L+6	0.539
362	0.224	H→L+4	0.406
Triplet→Triplet			
674	0.111	H-9→L(B)	0.716
582	0.412	H-11→L(B)	0.467

3.1 Excited States of SiPC-PEG_x (x=75,250)

Following the procedure described in section 2, several structures of SiPC-PEG structures with PEG mass of 75 and 250 were generated using the MD approach in the presence of water. Next, structures were optimized and the energy conformers differing significantly in energetic values were used for subsequent excited states calculations. Figure 2a, presents a snapshot from the MD computation and figure 2b illustrates the SiPC-PEG₇₅ conformer that differs in energy by 2.0 kcal/mol from that presented in figure 1. Figure 2c presents two SiPC-PEG₂₅₀ conformers differing in energy of 4.1 kcal/mol. In addition, snapshots from MD simulations were selected with several (3) water molecules within 5 Å of the SiPC-PEG₇₅ conformer.

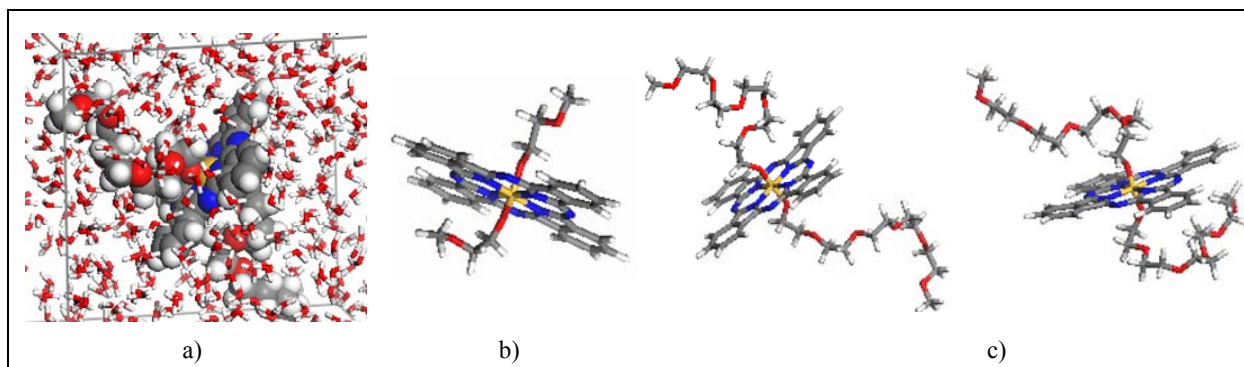


Figure 2. Unit cell of SiPC-PEG₂₅₀ with 500 water molecules (a), conformers of SiPC-PEG₇₅ (b), and SiPC-PEG₂₅₀ (c).

Table 3 presents the main excitation energies for selected conformers, c1 and c2. The B3LYP/6-31G*//PBE/DNP level of theory was used. The ZINDO(CIS=10)/INDO2//PBE/DNP results are also reported in table 3 for selected conformers. Comparison of major excitation peaks indicates that the conformation of PEG chain does not affect either the UV-Vis or RSA spectra. Including explicit water molecules also does not appear to significantly affect the spectral results. The spectra obtained with the short PEG chain (75) and the long PEG chain (250) are also very similar. This is in line with experimental measurements, obtained for a longer PEG chains with mass of 550 and 750 (Huang et al., 2004). Experimental results indicate an intense and sharp Q band at about 671 nm and a B band at about 354 nm. These values can be compared to our findings of about 620 and 340 nm, respectively. Although this level of DFT calculations leads to a blue shifted Q band, the B band matches closely the experimental results. The ZINDO spectrum matches closely to the experimental data, particularly for the Q band.

Table 3. Main excitation energies (in nm) and oscillator strength (f) from UV-Vis (Q and B bands) and RSA (R) calculations for SiPC-PEG_(x=75,250) complexes.

System\Excited state	Q	B	R
DFT			
c1 SiPC-PEG ₇₅	613 (0.37)	335 (0.54)	479 (0.31)
c2 SiPC-PEG ₇₅	613 (0.36)	337 (0.68)	477 (0.22)
c1 SiPC-PEG ₇₅ (3w)	611 (0.36)	334 (0.45)	516 (0.20)
c1 SiPC-PEG ₂₅₀	611 (0.35)	337 (0.47)	485 (0.25)
c2 SiPC-PEG ₂₅₀	611 (0.34)	338 (0.42)	500 (0.18)
ZINDO(CIS=10)/INDO2			
c2 SiPC-PEG ₇₅	671 (0.78)	327 (0.56)	—
c1 SiPC-PEG ₂₅₀	671 (0.78)	315 (1.66)	—
c2 SiPC-PEG ₂₅₀	670 (0.78)	316 (1.46)	—

We conclude that the UV-Vis and RSA spectral results are relatively insensitive to influences of the environment, as well as to the size and specific conformation of PEG. We confirm that the SiPC-PEG complex is green in color, and has primary RSA absorption in the visible range of the UV-Vis spectrum.

3.2 Effect of SiPC Stacking on Spectra

To elucidate further the impact of PEG on spectral properties, we performed calculations for various conformers of SiPC without PEG attached, with PEG attached on one side only, and including other substituents such as chlorine. The primary motivation for this investigation was to assess a possible color changes due to incomplete attachment of PEG fragments that may result in stacking of several PC rings. Figure 3 illustrates several structures with incomplete PEG attachment, while figure 4 (b-d) shows optimized structures used to study effects of stacking. Table 4 lists UV-Vis spectral results in the visual range of 400 to 700 nm, which includes the Q band of the PC complexes. The B3LYP/6-31G*//PBE/DNP DFT level of theory was used and the ZINDO(CIS=30)/INDO2//PBE/DNP semiempirical method was utilized for comparison.

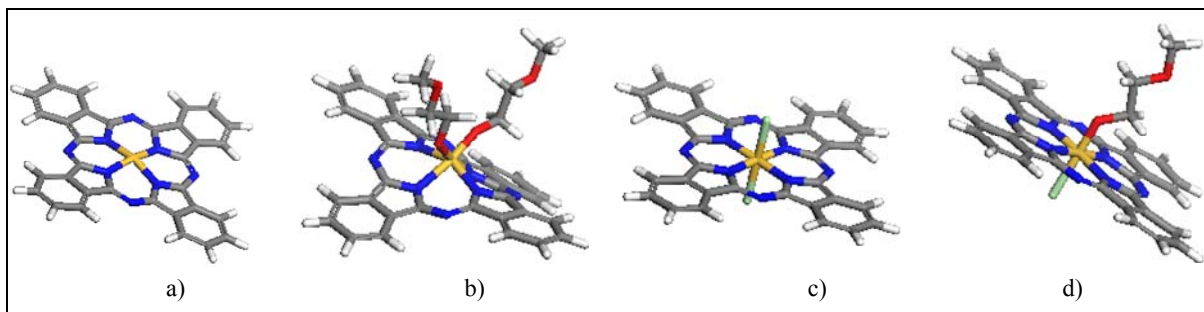


Figure 3. Conformers of SiPC with PEG₇₅ and Cl.

Table 4. Main excitation energies (in nm) and oscillator strength (f) in the visual range as calculated from DFT and ZINDO methods. Structures are shown in figure 3 (F3) and figure 4 (F4). Detailed explanation given in the text.

System\Excited State	DFT	ZINDO
F3a(D4h)	516 (0.67)	450 (2.69)
F3a(fromF3b)	667 (0.29)	780 (0.57)
F3b	658 (0.31)	774 (0.66)
F3c	620 (0.36)	717 (0.73)
F3d	617 (0.36)	713 (0.73)
F4a	626 (0.36)	710 (0.74)
F4b	523 (0.77)	517 (1.82)
F4c	536 (0.60)	497 (1.71)

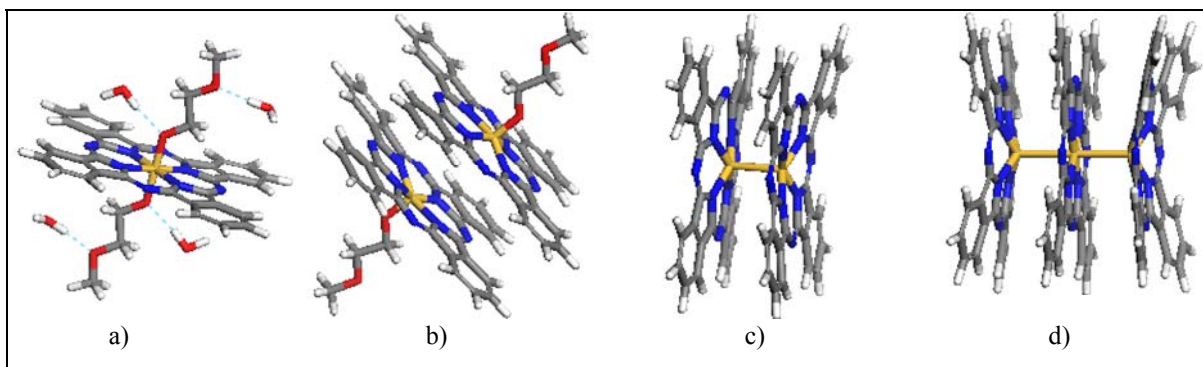


Figure 4. Structure of SiPC-PEG₇₅ with hydrogen-bonded water molecules and complexes of stacked SiPC fragments.

The trends in absorption spectrum as displayed in table 4 are similar for both the DFT and ZINDO results, although the absolute values of excitation energies are vastly different. Apparently substituting PEG oligomers with chlorine atom (figures 3c, 3d, and 2b) does not affect significantly the position of the Q band. Additionally, water molecules forming hydrogen bonds with the complex (structure F4a from figure 4a) also does not appear to significantly alter the spectral properties.

Distortion of the PC ring, such as displayed in figure 3b, shifts the spectrum towards the red. Structure F3b without the PEG oligomers (denoted as F3a [*from F3b*] in table 4) does not change the spectral results of the original F3b structure indicating that the PEG oligomers do not influence significantly the Q band. However, the Si-PC complex optimized under the D4h symmetry constraints shows a marked difference in spectral results. At the B3LYP/6-31G(d) level of theory, one finds several absorption energies in the green region, with a peak at 516 nm. The high symmetry of the SiPC structure leads to a much shorter Si-N bond, by almost 0.1 Å, as compared to structures with the PEG attached. The net charge on the central Si atom, according to the Hirschfeld analysis, is also markedly different and amounts to 0.55 as compared to about 0.42 for the F3b structure with PEG oligomers.

The effect of stacking has a significant effect on the color of the molecular system. Results in table 4 show a significant blue shift in the spectrum for structures F4b, F4c, and F4d (see figure 4). We note that the structure represented in F4d has yet to be calculated due to its size. Without the PEG oligomers attached, the SiPC rings tend to form an internal Si-Si bond, while for all stacked structures a strong π - π interaction is expected.

We conclude that the PEG oligomers affect the spectroscopy of SiPC system by imposing geometrical constraints and by minimizing stacking in the SiPC complexes. Upon attachment to the SiPC ring, PEG causes local deformation of the ring, increasing the Si-N distance and, in the case of non-symmetrical complexes such as F3d, extending the Si out of the PC plane. In the absence of axial substituents the Si atom transfers charge to the neighboring nitrogen atoms.

However, since both PEG and Cl atom withdraw electrons from the SiPC system and the net charge on the Si atom decreases, it indicates the charge flows from the PC ring through Si to the ligands. This rearrangement of electronic structure because of underlying geometrical changes causes the red shift of the Q band, thus making SiPC-PEG material transparent in the green part of the visual range.

4. Conclusions

In this report, we have evaluated various quantum chemistry methods for calculations involving structure and spectral results of a series of PEG complexes. In particular, UV-Vis and RSA spectra of Si-phthalocyanine complexes with axially attached PEG poly(ethylene oxide) have been investigated. Based on these computational studies, we find that GGA and LDA density functional approaches, using a computationally efficient algorithm of fitting density, reproduces well the UV-Vis spectrum found experimentally for complexes of this type. The ZINDO semiempirical method predicts very accurate UV-Vis spectra provided that the CIS expansion is short, and the underlying optimized structure is optimized using higher order quantum chemical methods, such as provided by density functional theory. Reliable results for RSA spectra can only be obtained using higher level computational methods, such as provided by the hybrid B3LYP method. The DFT methods require a modest basis set expansion, however, further study, including diffuse functions is ongoing to confirm this assessment. These conclusions are important for the study of much larger complexes including NCs and their derivatives.

We have found that the length of PEG oligomers, the particular conformational preference, as well as the water environment simulated with inclusion of explicit water molecules, does not significantly affect either the UV-Vis or RSA spectra. However, partial attachment of PEG oligomers to SiPC complex may lead to stacking of SiPC rings, significantly affecting UV-Vis spectral properties. The system will thereby no longer be transparent in the desirable green range of the spectrum.

The results of this report improve our understanding of the binding of PEG oligomers to SiPC complex and also may help in selecting axial substituents for synthesis of PCs with desirable optical properties.

5. References

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