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A Time-Dependent DFT Study on Band Gaps and Effective Conjugation Lengths of Polyacetylene, Polyphenylene, Polypentafulvene, Polycyclopentadiene, Polypyrrole, Polyfuran, Polysilole, Polyphosphole, and Polythiophene

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ABSTRACT: The chain length dependence of excitation energies of oilgomers of polyene, *p*-phenylene, pentafulvene, cyclopentadiene, pyrrole, furan, silole, phosphole, and thiophene was studied employing the time-dependent density functional theory with B3LYP functional. Band gaps and effective conjugation lengths of the corresponding polymers were obtained by extrapolating vertical excitation energies of trimers through pentamers to infinite chain length. Polypentafulvene, polycyclopentadiene, polysilole, and polyphosphole were predicted to have smaller band gaps than polythiophene, and polypentafulvene has the smallest band gap. Among the studied cyclopentadiene-based polymers, those with the third row heteroatoms were found to have narrower band gaps than their second row counterparts.

1. Introduction

Intensive research has been dedicated to exploring novel conjugated polymers with narrow band gaps, E_g, a property that is essential for high conductivity upon doping, high nonlinear optical response, and the possible transparency in the visible region of the absorption spectrum, etc.[1,2] Here, we quote E_g as the measured longest wavelength electronic absorption maximum, λ_{max},[1] of polymeric systems, although in many literatures it was also interpreted as the threshold of photoemission or the threshold of photoconduction. *trans*-Polyacetylene (*t*-PA), **1a**, is a fundamental model of organic conjugated conductors with the opening of a band gap around 1.8 eV,[3] owing to the Peierls' distortion in its infinite chain. Other known polyaromatic polymers include poly(*p*-phenylene) (PPP) (X = −(CH=CH)−), poly(thiophene) (PTh) (X = S), and poly(pyrrole) (PPy) (X = NH), which can be viewed as the *cis*-polyacetylene (**1b**) carbon chains stabilized by group X (Scheme 1).[2] Among them, PTh and its derivatives have band gaps of around 2.20 eV,[2] appreciably smaller than those of PPy (2.85 eV)[4] and of PPP (3.40 eV),[5] and thus attracted considerable experimental and theoretical interest.[2,6,7] Among synthetic strategies for generating a narrow band gap, a possible approach is the modification of π-conjugated polymers with the main group elements such as silicon and phosphorus.[8−10] Up to now, less is known experimentally about such polymers. Obviously, a theoretical investigation on the band gaps of these polymers is very instrumental in guiding the experimental synthesis, which is the topic of the present work.

Theoretical studies on the electronic structures of polymers have contributed a lot to rationalize the properties of known polymers[11−18] and to predict those of yet unknown ones.[19] There are two different theoretical approaches to evaluate the band gaps of polymers. One is the polymer approach in which the periodic structures are assumed for infinite polymers. Another one, the oligomer extrapolation technique,[16,17,19] has acquired the increasing popularity in this field, however. In this approach, a sequence of increasing longer oligomers is calculated, and extrapolation to infinite chain length is followed. A distinct advantage of this approach is that it can provide the convergence behavior of the structural and electronic properties of oligomers. In practice, both the oligomer extrapolation and the polymer approaches are generally considered to be complementary to each other in our understanding of the properties of polymers.

The theoretical quantity for direct comparison with experimental band gap should be the transition (or excitation) energy from the ground state to the first dipole-allowed excited state. There exist a variety of theoretical approaches for evaluating this quantity for oligomers as well as infinite polymers. The crudest estimate is the orbital energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), obtained from Hartree−Fock (HF) or density functional theory (DFT) calculations.[18,19] The implicit assumption underlying this approximation is that the lowest singlet excited state can be described by only one singly excited configuration in which an electron is promoted from HOMO to LUMO. In addition, the orbital energy difference between HOMO and LUMO is still an approximate estimate to the transition energy since the transition energy also contains significant contributions from some two-electron integrals. However, the real situation is that an accurate description of the lowest singlet excited state requires a linear combination of a number of excited configurations, although the one mentioned above often plays a dominant role. The calculated HOMO−LUMO gap agrees fairly well with the experimental band gap in many cases;[19] it may probably due to the error cancellations. Hence, it is desirable to obtain more rigorous information on the nature of the lowest singlet excited state by employing other elaborate theoretical methods. Among those theories, Hartree−Fock (HF)-based methods such as configuration interaction singles (CIS)[20] and the random phase approximation (RPA),[21] which is equivalent to the time-

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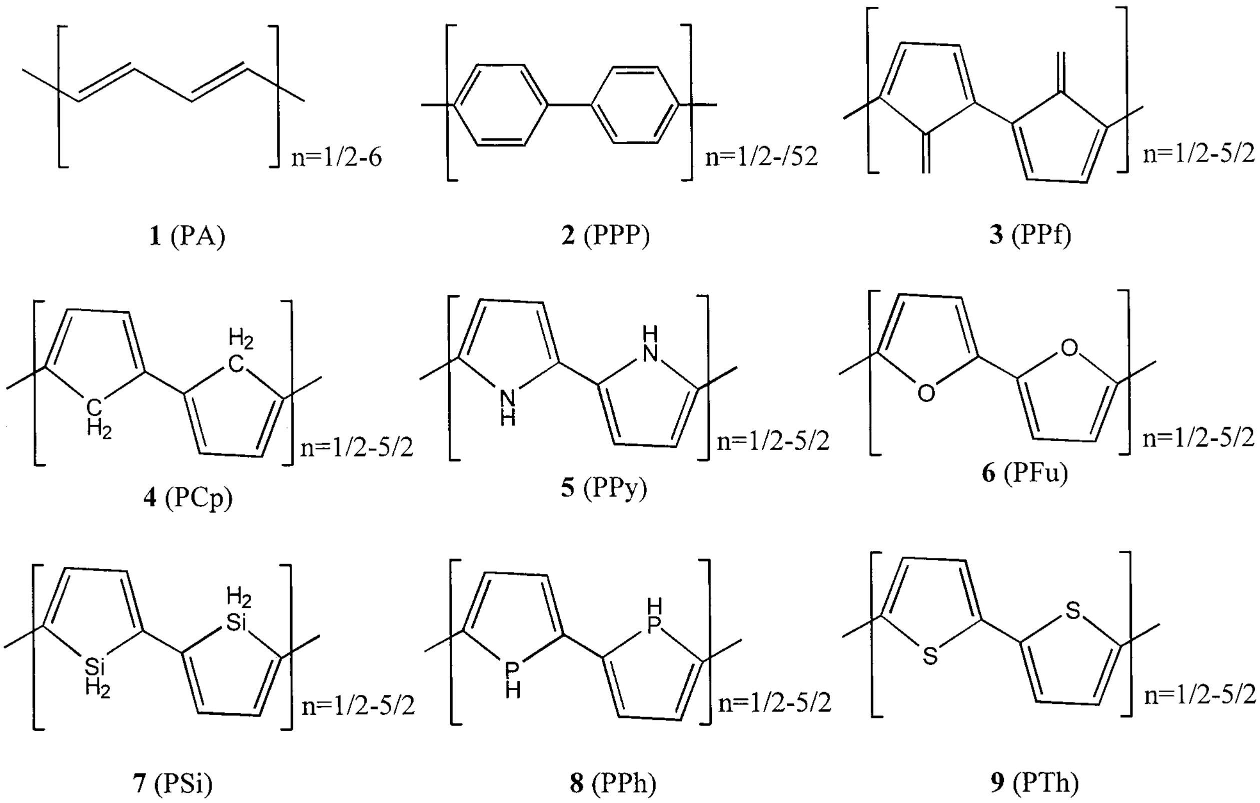
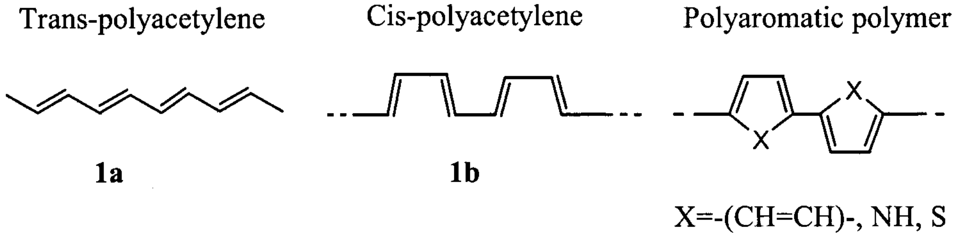


Figure 1. Structures of the studied oligomers.

Scheme 1



dependent HF (TDHF),[22] usually only provide the qualitative or semiquantitative descriptions for the low-lying excited states. Time-dependent density functional theory (TDDFT) is a recently developed tool for calculating excitation energies.[23,24] A significant quantitative improvement in the excitation energies from TDDFT over those from HF-based methods has been demonstrated, but at roughly comparable computational cost.[23,24] However, as pointed out by Hirata, Head-Gordon, and Bartlett,[25] for infinite polymers or sufficiently large systems the excitation energies to the lowest singlet excited states calculated by TDDFT with the pure exchange-correlation functionals are not better than the corresponding HOMO−LUMO gaps because they tend to converge to the same value. The failure of TDDFT with the pure exchange-correlation functionals in the large systems is attributed to the fact that the exchange-correlation potentials generated by the current approximate exchange-correlation functionals decay too rapidly in the asymptotic region. This problem is partially overcome in TDDFT with the HF/DFT hydrid functionals such as B3LYP, since the incorporated HF exchange potential decays correctly. Test calculations on polyethylene and sufficiently large *n*-alkanes demonstrated that the excitation energies to the lowest singlet excited states calculated using TDDFT with the B3LYP functional do not converge to the corresponding HOMO−LUMO gaps.[25] For linear oligoenes, recent studies on the excited energies of the first dipole-allowed ^{1}Bu states also showed that TDDFT calculations with the B3LYP functional can correctly reproduce the general trend of decreasing excitation energy with chain length, with a systematic underestimation of only approximately 0.3−0.5 eV.[23,26] To conclude from the above discussions, TDDFT with the B3LYP functional is expected to be a relatively reliable tool for evaluating the excitation energies of the low-lying excite states for small- and medium-sized molecules.

In this paper, we employ TDDFT with the B3LYP functional to investigate the chain-length dependence of the vertical excitation energies of several heterocyclopentadiene oligomers (Figure 1) including some less investigated systems, oligo(pentafulvene)s, oligo(cyclopentadiene)s, oligo(polysilole)s, and oligo(phosphole)s, and predict their band gaps of the corresponding polymers by extrapolation. Hereafter, TDDFT with the B3LYP functional is abbreviated as TDDFT for simplicity. In addition, calculations on oligomers are also very useful in their own right since well-defined oligomers may sever as potential components in future molecular scale electronic devices. These calculations allow the determination of how molecular properties of oligomers converge with increasing chain length to yield those of the corresponding infinite polymers. In fact, a useful concept, effective conjugation length (ECL), the number of repeat units at which saturation of a property occurs,[7] can also be estimated from calculations on a series of oligomers. We will estimate the ECL for all selected oligomers based on the convergence of the calculated excited energy of the first dipole-allowed excited state with the increasing chain length. Apart from the selected heterocyclopentadiene oligomers, well-studied oligomers such as those of *t*-PA, PPP, PTh, and PPy are also reexamined with TDDFT for further validating the theory and for comparison. The results obtained for them will be discussed only briefly.

It should be mentioned that for some selected heterocyclopentadiene oligomers Salzner et al.[19] predicted the band gaps of the corresponding polymers based on the extrapolated HOMO−LUMO gaps with DFT hybrid method. For some conjugated polymers, Brédas et al.[11] estimated their band gaps using the above strategy and the valence effective Hamiltonian (VEH) technique, while Lahti et al.[16] obtained their band gaps by extrapolating the transition energies of oligomers obtained with the PPP-CI method. In addition, energy gaps of substituted oligothiophenes up to hexamers have been recently estimated using semiempirical, HF, and DFT methods.[18] In these studies, good agreement was generally found between the predicted and observed band gaps for the studied polymers, partially due to error cancellations or efficient parametrizations in VEH and PPP models. Different from these investigations, the main features of this work are (1) TDDFT is first applied to predict the band gaps for a wide range of conjugated heterocyclopentadiene-based polymers and (2) the ECLs of these polymers are tentatively estimated.

2. Computational Details

The ground-state geometries of oligomers were fully optimized using the density functional theory (DFT), B3LYP/6-31G(d), as implemented in Gaussian 98.[27] TDDFT (B3LYP) calculations of the excitation energies were then performed at the optimized geometries of the ground states. We have investigated the basis set dependence of excitation energies calculated with TDDFT for polyene oligomers up to quatermer. The results showed that for all oligomers the excitation energies from the ground states to the ^{1}Bu states with 6-31+G(d) agree within 0.01 eV with those with much larger basis set 6-311++G(d,p). Thus, 6-31+G(d) (for all atoms) is used in all TDDFT calculations.

Band gaps of polymers were obtained by plotting the vertical excitation energies for the first dipole-allowed excited states of trimers through pentamers against reciprocal chain lengths and extrapolating to infinite chain length. The ECL was estimated by the convergence of excitation energies with the chain length within a threshold of 0.01 eV, based on the obtained linearity between the excitation energy and reciprocal chain length.

Table 1. Excitation Energies (eV) of Oligomers 1−9

oligomer	TDDFT	exptl	oligomer	TDDFT	exptl
t-PA (**1**)			PPy (**5**)		
$n = {}^{1}/_{2}$	7.20	7.65^{a}	$n = {}^{1}/_{2}$	5.73	5.96^{a}
$n = 1$	5.63	5.92^{b}	$n = 1$	4.40	4.35^{a}
$n = {}^{3}/_{2}$	4.65	4.95^{c}	$n = {}^{3}/_{2}$	3.87	3.59^{a}
$n = 2$	3.99	4.41^{d}	$n = 2$	3.33	
$n = {}^{5}/_{2}$	3.52	4.02^{e}	$n = {}^{5}/_{2}$	3.07	
$n = 3$	3.17	3.4^{a}	$E_g(n{=}\infty)$	1.95	2.85^{i}
$n = {}^{7}/_{2}$	2.89		PFu (**6**)		
$n = 4$	2.67		$n = {}^{1}/_{2}$	6.31	
$n = {}^{9}/_{2}$	2.48		$n = 1$	4.37	
$n = 5$	2.33		$n = {}^{3}/_{2}$	3.56	
$n = {}^{11}/_{2}$	2.20		$n = 2$	3.12	
$n = 6$	2.09		$n = {}^{5}/_{2}$	2.82	
$E_g(n{=}\infty)$	1.32	1.8^{f}	$E_g(n{=}\infty)$	1.69	2.35^{j}
PPP (**2**)			PSi (**7**)		
$n = {}^{1}/_{2}$	5.41	5.90^{a}	$n = {}^{1}/_{2}$	4.32	
$n = 1$	4.87	4.92^{a}	$n = 1$	3.11	
$n = {}^{3}/_{2}$	4.29	4.34^{g}	$n = {}^{3}/_{2}$	2.48	
$n = 2$	3.96	4.11^{g}	$n = 2$	2.10	
$n = {}^{5}/_{2}$	3.76		$n = {}^{5}/_{2}$	1.84	
$E_g(n{=}\infty)$	2.97	3.4^{h}	$E_g(n{=}\infty)$	0.86	
PPf (**3**)			PPh (**8**)		
$n = {}^{1}/_{2}$	3.27		$n = {}^{1}/_{2}$	4.66	
$n = 1$	2.54		$n = 1$	3.29	
$n = {}^{3}/_{2}$	1.79		$n = {}^{3}/_{2}$	2.65	
$n = 2$	1.53		$n = 2$	2.28	
$n = {}^{5}/_{2}$	1.35		$n = {}^{5}/_{2}$	2.03	
$E_g(n{=}\infty)$	0.70		$E_g(n{=}\infty)$	1.08	
PCp (**4**)			PTh (**9**)		
$n = {}^{1}/_{2}$	5.04		$n = {}^{1}/_{2}$	5.76	5.37^{a}
$n = 1$	3.40		$n = 1$	3.87	4.12^{a}
$n = {}^{3}/_{2}$	2.67		$n = {}^{3}/_{2}$	3.23	3.52^{a}
$n = 2$	2.27		$n = 2$	2.81	
$n = {}^{5}/_{2}$	2.00		$n = {}^{5}/_{2}$	2.56	
$E_g(n{=}\infty)$	0.98		$E_g(n{=}\infty)$	1.52	2.20^{k}

[a] Reference 11 and references therein. [b] Reference 32. [c] Reference 33. [d] Reference 34. [e] Reference 35. [f] Reference 3. [g] Reference 37. [h] Reference 5. [i] Reference 4. [j] Reference 36. [k] Reference 2.

3. Results and Discussion

The TDDFT vertical excitation energies of oligomers and estimated band gaps for corresponding polymers **1**−**9** (Figure 1) are presented in Table 1. Compared with the available experimental excitation energies for oligomers of *t*-PA, PPP, PPy, and PTh, the average deviation of the calculated values is 0.28 eV, confirming that TDDFT with B3LYP functional can give relatively accurate predictions on vertical excitation energies for a variety of molecules. The linearity between the calculated excitation energies and the inverse chain length is excellent for various homologous series of oligomers. By extrapolating the resultant linear relationship to infinite chain length, the band gap and ECL of the corresponding polymer are predicted. From Table 1, one can see that the TDDFT predictions systematically underestimate the band gaps of those known polymers, with the average deviation of about 0.63 eV. Two factors may be responsible for this relatively large error. One is that calculations on a few longer oligomers may be required so that more data could be used in linear regression. Another is that the predicted band gaps are for isolated gas-phase chains, while experimental band gaps are usually measured in the condensed phase where interchain interactions may be significant. However, the decreasing trend in E_g in the order PPP > PPy > PFu > PTh > *t*-PA is well reproduced by the TDDFT predictions. In fact, there exists a good linear correlation between the predicted band gaps and the experimental observations as shown in Figure 2. Therefore, the TDDFT band gaps can still convey very useful information for designing novel polymers with narrow band gaps.

Despite the good agreement between the calculated excitation energies and the experimental data, it is also

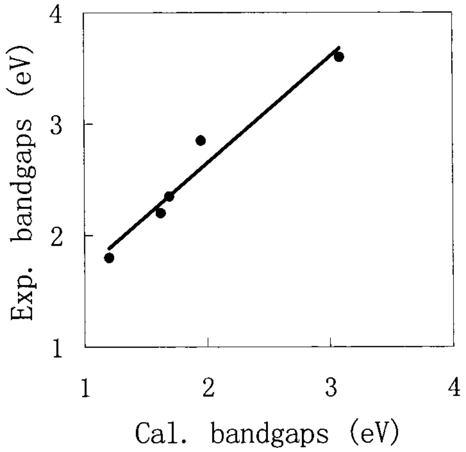


Figure 2. Band gaps (eV) estimated from TDDFT calculations vs the experimental data.

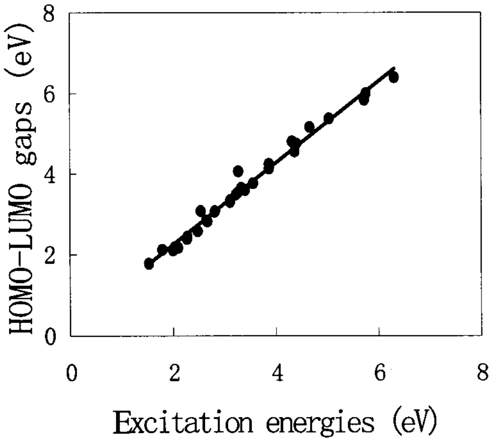


Figure 3. Correlation between the excitation energies (eV) and the HOMO−LUMO gaps (eV).

necessary to check the validity of these excitation energies calculated by TDDFT. Previous studies showed that the excitation energies calculated by TDDFT with the current exchange-correlation functionals are not reliable when the calculated excitation energies are higher than the negative of the HOMO energies. In addition, it is interesting to compare the TDDFT excitation energies and the corresponding HOMO−LUMO gaps. For all molecules under consideration, we have displayed in Table 2 the negative of HOMO energies, the HOMO−LUMO gaps, and the TDDFT excitation energies. From Table 2, one can see that in all cases the TDDFT excitation energies are below the negative of HOMO energies and thus may be numerically reliable. Interestingly, there is a linear correlation between the TDDFT excitation energies and HOMO−LUMO gaps, as exhibited in Figure 3, so the HOMO−LUMO gap approach can also be used to provide valuable information on the band gaps of oligomers and polymers. For oligomers of t-PA, PPf, PCp, PSi, and PPh with narrow band gaps, the TDDFT excitation energies and the HOMO−LUMO energies seem to converge quickly to the same limit, reflecting the influence of the incorrect asymptotic behavior of the pure exchange-correlation potential included in the B3LYP potential. While we notice that appreciable differences between the TDDFT transition energies and the HOMO−LUMO separations exist for oligomers with large band gaps such as PPP and PPy. For oligomers studied in this work, TDDFT with the B3LYP functional does quite well in predicting the excitation energies to the lowest excited singlet states. However, unlike the simple HOMO−LUMO gap approach, TDDFT calculations are still computationally expensive and difficult to treat even larger systems.

In the following, we will discuss the predicted band gaps and ECLs in some detail for all conjugated systems shown in Figure 1. First, the results of *t*-PA are briefly presented. Then, the properties of the less investigated

Table 2. TDDFT Excitation Energies, HOMO−LUMO Gaps (Δ_{H-L}), and the Negative of HOMO Energies ($-\epsilon_{HOMO}$) of Oligomers 1−9 (in Units of eV)

oligomer	TDDFT	Δ_{H-L}	$-\epsilon_{HOMO}$	oligomer	TDDFT	Δ_{H-L}	$-\epsilon_{HOMO}$
t-PA (**1**)				PPy (**5**)			
$n = {}^{1}/_{2}$	7.20	7.37	7.56	$n = {}^{1}/_{2}$	5.73	5.83	5.87
$n = 1$	5.63	5.45	6.53	$n = 1$	4.40	4.75	5.02
$n = {}^{3}/_{2}$	4.65	4.40	5.99	$n = {}^{3}/_{2}$	3.87	4.24	4.78
$n = 2$	3.99	3.74	5.65	$n = 2$	3.33	3.65	4.48
$n = {}^{5}/_{2}$	3.52	3.28	5.42	$n = {}^{5}/_{2}$	3.07	3.40	4.37
$n = 3$	3.17	2.95	5.26	PFu (**6**)			
$n = {}^{7}/_{2}$	2.89	2.70	5.13	$n = {}^{1}/_{2}$	6.31	6.39	6.45
$n = 4$	2.67	2.50	5.03	$n = 1$	4.37	4.55	5.58
$n = {}^{9}/_{2}$	2.48	2.34	4.95	$n = {}^{3}/_{2}$	3.56	3.76	5.22
$n = 5$	2.33	2.21	4.88	$n = 2$	3.12	3.35	5.04
$n = {}^{11}/_{2}$	2.20	2.10	4.83	$n = {}^{5}/_{2}$	2.82	3.05	4.91
PPP (**2**)				PSi (**7**)			
$n = {}^{1}/_{2}$	5.41	6.62	7.00	$n = {}^{1}/_{2}$	4.32	4.80	6.52
$n = 1$	4.87	5.26	6.33	$n = 1$	3.11	3.30	5.67
$n = {}^{3}/_{2}$	4.29	4.67	6.04	$n = {}^{3}/_{2}$	2.48	2.58	5.28
$n = 2$	3.96	4.36	5.89	$n = 2$	2.10	2.17	5.07
$n = {}^{5}/_{2}$	3.76	4.17	5.80	$n = {}^{5}/_{2}$	1.84	1.90	4.93
PPf (**3**)				PPh (**8**)			
$n = {}^{1}/_{2}$	3.27	4.06	6.12	$n = {}^{1}/_{2}$	4.66	5.16	6.54
$n = 1$	2.54	3.08	5.39	$n = 1$	3.29	3.57	5.67
$n = {}^{3}/_{2}$	1.79	2.12	4.85	$n = {}^{3}/_{2}$	2.65	2.85	5.29
$n = 2$	1.53	1.78	4.66	$n = 2$	2.28	2.44	5.09
$n = {}^{5}/_{2}$	1.35	1.55	4.56	$n = {}^{5}/_{2}$	2.03	2.18	4.95
PCp (**4**)				PTh (**9**)			
$n = {}^{1}/_{2}$	5.04	5.37	6.07	$n = {}^{1}/_{2}$	5.76	5.99	6.54
$n = 1$	3.40	3.59	5.17	$n = 1$	3.87	4.13	5.67
$n = {}^{3}/_{2}$	2.67	2.82	4.40	$n = {}^{3}/_{2}$	3.23	3.49	5.29
$n = 2$	2.27	2.39	4.77	$n = 2$	2.81	3.06	5.09
$n = {}^{5}/_{2}$	2.00	2.11	4.54	$n = {}^{5}/_{2}$	2.56	2.18	4.95

systems are evaluated in comparison with the structurally similar systems PPP, PPy, and PTh.

***t*-PA.** We have calculated the vertical excitation energies of the first optically allowed states for oligoenes up to 12 monomers (Table 1). From the linearity obtained by plotting the results of 3−12 monomers against reciprocal monomer number, the band gap of *t*-PA is predicted to be 1.32 eV, 0.48 eV less than the experimental value. The estimated ECL of *t*-PA is $n_{\mathrm{ECL}} \approx 32$, in good agreement with the estimate of 38 from optical properties of PA films.[28]

PPP and PPf (Polypentafulvene). Pentafulvene is known as nonaromatic, quite different from its constitutional isomer, benzene.[29,30] The geometry of pentafulvene from microwave spectra is well reproduced by the present DFT calculation.[30] The dramatic difference between these two isomeric monomers also preserves in the electronic structures of their corresponding polymers, PPP (**2**) and PPf (**3**). In PPP oligomers, steric interactions between ortho-H atoms cause the planes of neighboring aryl rings to adopt dihedral angles around 38°, which significantly reduces the π-orbital overlap and thus prevents extended π-conjugation. In contrast, PPf oligomers all have planar ground-state structures and much lower excitation energies than those of their PPP analogues. The extrapolated band gap of PPf is 0.70 eV (Table 1), only about one-quarter of the predicted value of PPP. It is the lowest band gap among all conjugated polymers studied in this work. The saturation of excitation energies of oligomers with the chain length is estimated to occur at around 20 and 18 monomers for PPP and PPf, respectively.

Polycyclopentadiene (PCp) and Polysilole (PSi). Both PCp (**4**) and PSi (**7**) have not been widely investigated experimentally yet. For the first dipole-allowed excited state of cyclopentadiene the TDDFT transition energy is 245.79 nm (5.04 eV), falling well into the range between 238 and 250 nm observed for the maximum of the absorption of cyclopentadiene and its C-methylated derivatives.[31] TDDFT predicts the lowest excited state of silole at longer wavelength of 286.39 nm (4.32 eV), which is consistent with the absorption maximum region around 285 nm measured for its C- and H-methylated derivative.[31] Small band gaps of 0.98 eV for PCp and 0.86 eV for PSi have been predicted by the present TDDFT calculations (Table 1). With the extension in monomer numbers, excitation energies of PCp and PSi are estimated to be nearly constant after 23 and 22 monomers, respectively.

Polypyrrole (PPy) and Polyphosphole (PPh). Little study has been done on PPh,[10] although the lower periodic analogue, PPy, has attracted extensive experimental and theoretical interests.[1,7,11] The estimated band gap is 1.08 eV for PPh, almost half of that for PPy according to the present TDDFT computations. A little faster convergence of excitation energies appears in PPh ($n_{\mathrm{ECL}} \approx 21$) than in PPy ($n_{\mathrm{ECL}} \approx 24$).

Different from other aromatic oligomers, the transitions from the ground states 1 ^{1}Ag to the first excited singlet states (2 ^1A_g) of pyrrole (4.90 eV) and dipyrrole (4.03 eV) are optically forbidden with the vanishing oscillator strength from the present work. The second excited singlet states are dipole-allowed, which correspond to the observed maximum wavelength in absorption spectra. For the monomer and dimer the calculated optically allowed excitation energies of 5.73 and 4.40 eV agree well with the experimental values of 5.96 and 4.35 eV,[11] respectively. While for tripyrrole and larger oligomers, the lowest excited state turns out to be the dipole-allowed 1 Bu^1 state. A good agreement between our theoretical lowest excitation energy of 3.87 eV and the observed value of 3.59 eV[11] for tripyrrole has been attained.

Similar to the experimental observations[10] as well as the DFT calculations by Salzner et al.,[19] the puckered geometry of the PPh have also been found in the present study. In addition, our calculations show a slight preference of the conformer with all syn-disposition of H atoms bonded with P to that alternating disposition one as shown in Figure 4. The slight geometrical difference between these two kinds of conformers results in about 0.10 eV difference in their excitation energies (Figure 4).

Polyfuran (PFu) and Polythiophene (PTh). Our TDDFT calculations suggest a relative small band gap of 1.52 eV for PTh, 0.17 eV narrower than the predicted band gap of PFu. The ECL of PFu is extrapolated at around 23 monomers. For PTh, a slightly shorter ECL at 22 monomers is estimated, being close to the UV/vis related $n_{\mathrm{ECL}} \approx 17$ deduced from oligo(α-thiophene)s and $n_{\mathrm{ECL}} \approx 20$ from the derivative of PTh.[7]

PTh and many PTh-based polymers have been found growing interest in semiconducting materials and device applications. From the above results, novel polymers, PPf, PCp, PSi, and PPh, were predicted to have smaller band gaps than PTh, which is the reference for the evaluation of new strategies for gap reduction. Thus, they may be the targets for experimental syntheses.

Periodic Trends of Band Gaps. According to the row and group of bridging heteroatoms in the periodic table, the band gaps of the studied heterocyclopentadiene-based polymers **4**−**9** were classified in Figure 5, from which we find that (1) polymers with higher periodic elements tend to have narrower band gaps, e.g., PSi < PCp, PPh < PPy, and PTh < PFu, and (2) polymers with the third row elements, Si, P, and S, the band gaps increase with the number of their lone pairs, i.e., in the order of PSi < PPh < PTh, while such a trend in the second row atoms is interrupted by the largest band gap of PPy. Similar trends of band gaps of these polymers have also been pointed out on the basis of the calculated HOMO−LUMO gaps by Salzner et al.[19] The studied cyclopentadiene-based polymers have similar ECLs of around 21−24 monomers. The higher periodic elements, such as Si, P, and S, may cause a little faster convergence in their excitation energies than the corresponding second row atoms. The effort to gain a theoretical understanding of the whole periodic trends of band gaps is still underway.

4. Conclusions

The chain length dependence of excitation energies of oilgomers of polyene, *p*-phenylene, pentafulvene, cyclopentadiene, pyrrole, furan, silole, phosphole, and thiophene was studied employing the time-dependent density functional theory with B3LYP functional. Band gaps of the corresponding polymers were obtained by extrapolating excitation energies of trimers through pentamers to infinite chain length. Compared with the available experimental values, the decreasing trend in E_g in the order PPP > PPy > PFu > PTh > *t*-PA is well reproduced by the TDDFT predictions. The estimated effective conjugation lengths for the studied polymers

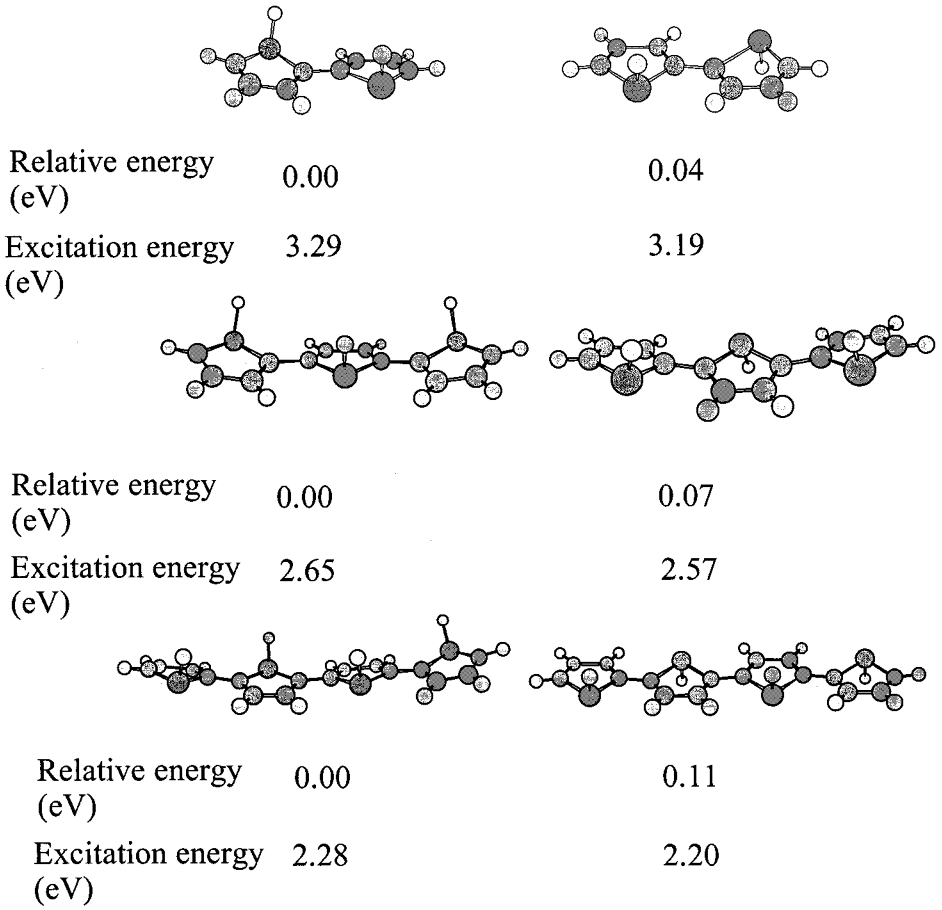


Figure 4. Relative stabilities and excitation energies (in units of eV) of conformers of PPh oligomers.

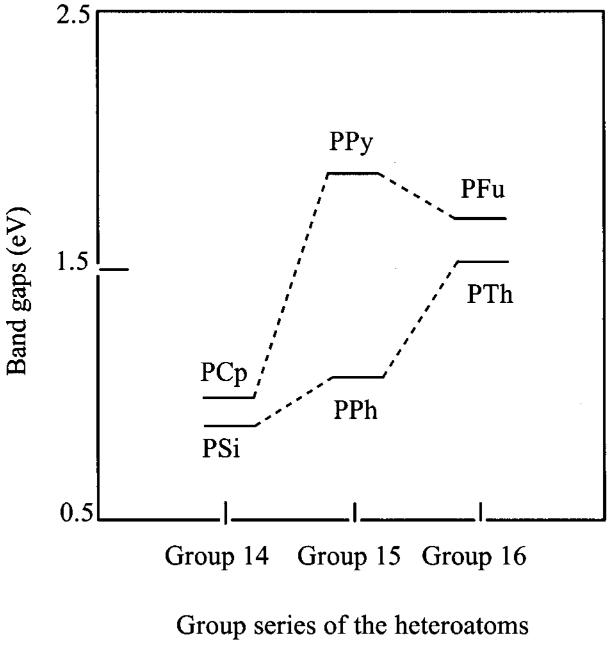


Figure 5. Periodic trends of band gaps of polymers **4**−**9**.

are in good agreement with experimental data where available. PPf, PCp, PSi, and PPh are suggested to be good candidates for novel conducting or optical materials because their band gaps are smaller than that of the well-studied PTh. The periodic trends in band gaps observed for poly(heterocyclopentadiene)s may be useful for the future design of conducting polymers.

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