Theor Chem Acc (2010) 125:35–44
DOI 10.1007/s00214-009-0655-4

REGULAR ARTICLE

Understanding on absorption and fluorescence electronic transitions of carbazole-based conducting polymers: TD-DFT approaches

**Songwut Suramitr · Wichanee Meeto ·
Peter Wolschann · Supa Hannongbua**

Received: 7 May 2009 / Accepted: 5 October 2009 / Published online: 30 October 2009

Abstract The electronic excitation transitions of carbazole-based oligomers, (Cz-co-Cz)$_N$, (Cz-co-Fl)$_N$ and (Cz-co-Th)$_N$ ($N = 2$–4) were investigated using density functional theory (DFT) and time-dependent (TD) DFT methods. Our results show that the calculated ground state geometries favor a more aromatic, planer structure, while the electronically excited geometries favor a quinoidic type structure. Absorption and fluorescence energies have been obtained from TD-B3LYP/SVP calculations performed on the S$_1$ optimized geometries and are in excellent agreement with experimental data. The experimental fluorescence excitation energies for (Cz-co-Cz)$_4$, (Cz-co-Fl)$_4$ and (Cz-co-Th)$_4$ (2.76, 2.63, and 2.25 eV, respectively) correspond closely with the predicted S$_1$ transitions (2.84, 3.91 and 2.43 eV, respectively). We also report the predicted radiative lifetimes 0.52, 0.47, and 0.99 ns for (Cz-co-Cz)$_N$, (Cz-co-Fl)$_N$ and (Cz-co-Th)$_N$, discuss the origin of the small stoke shift of the carbazole based oligomers and the magnitude of bathochromic shifts. We conclude by discussing the benefits of theoretical calculations, which can provide critical structural and electronic understanding of excitation–relaxation phenomena that can be exploited in design of novel optical materials.

Keywords Carbazole-based · Density functional theory · TDDFT · Radiative lifetimes

1 Introduction

Conducting polymers as light-emitting diodes, field effect transistors, charge storage devices, photodiodes, sensors, etc. [1, 2] are currently of interest. In the last year, novel well-defined 2,7-carbazole-based (Cz) polymers were synthesized by Leclerc et al. [2–7]. 2,7-Carbazole-based polymers and derivatives with thiophene, pyrrole, phenylene, and fluorene subunits have been synthesised [8–10], are currently of both industrial and academic interest because of their wide-ranging potential in electronic devices. These novel polymeric materials are stable in air and soluble in many usual organic solvents. Interestingly, the absorption and fluorescence spectra of these materials exhibit significant differences [11–13]. It is found that the existence of multi-components in the fluorescence decay profiles of such polymers in the solid state is caused by several distinct intermolecular π–π* interactions. However, these interactions are not strong enough to provoke the appearance of distinct fluorescence bands or even to increase the bandwidths of the emission bands in solution. Fundamental understanding on structural and energetic properties of this kind of copolymers could lead to beneficial knowledge for the design of novel copolymers. Therefore, it is of interest to compare the absorption and fluorescence transitions of 2,7-carbazole-based polymers and its dependence on the structural and the electronic properties. We are also interested in exploring the

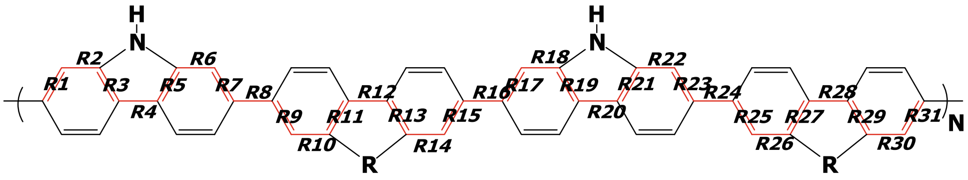
---

S. Suramitr · W. Meeto · S. Hannongbua
Department of Chemistry, Faculty of Science,
Kasetsart University, Bangkok 10900, Thailand
e-mail: fscisph@ku.ac.th

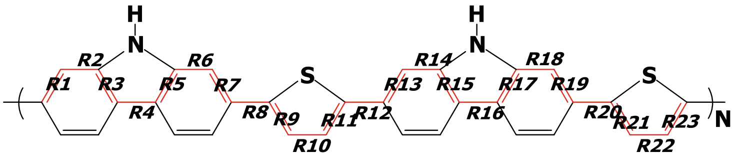
S. Suramitr (✉) · W. Meeto · S. Hannongbua
The Center of Nanoscience, Kasetsart University,
Bangkok, 10900, Thailand
e-mail: fsciswsm@ku.ac.th

P. Wolschann
Institute for Theoretical Chemistry, University of Vienna,
Währinger Straße 17, 1090 Vienna, Austria

Fig. 1 Structures and numbering schemes of **a** (Cz-co-Cz)$_N$ and (Cz-co-Fl)$_N$ and **b** (Cz-co-Th)$_N$ oligomers



(a) R=NH: -(Cz-co-Cz)$_N$- and R=CH_2: -(Cz-co-Fl)$_N$-



(b) -(Cz-co-Th)$_N$-

excitation mechanism since this will affect the pattern of the emission bands.

In previous studies of carbazole-based molecules [11–13], calculations were performed using DFT as well as (TD-DFT) with the B3LYP functional and three basis sets: 6-31G, 6-31G(*d*) and 6-311G(*d*,*p*). However, only ground state conformational analysis and calculations of the vertical excitation energies were carried out. From these calculations, it was reported that the optimized ground state geometries of oligomers with six-membered heterocyclic rings copolymers are nonplanar, whereas planar copolymer structures were found for with five-membered heterocyclic ring a results of the subtle balance between minimizing steric repulsion and maximizing electronic conjugation [14].

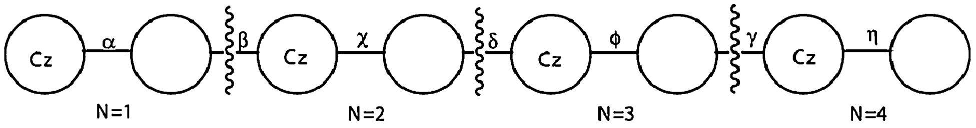
To increase our understanding of this important polymer class, we have performed calculations on the excited state properties of carbazole-based homopolymers and copolymers with fluorene and thiophene substituents (formulas are given in Fig. 1). In this study, we put particular emphasis on understanding the ground and low-lying excited states of the carbazole-homopolymer (Cz-co-Cz)$_N$, carbazole-co-fluorene (Cz-co-Fl)$_N$ and carbazole-co-thiophene (Cz-co-Th)$_N$ oligomers, which are explored by theoretical studies. The transitions associated with the absorption and fluorescence spectra of carbazole-based oligomers are explored. The fluorescence energies and radiative lifetimes are also analyzed in an attempt to gain better, more general understanding of the behavior of such systems.

2 Computational details

All QM calculations were performed using TURBOMOLE version 5.7 [15]. All geometry optimizations were performed using TURBOMOLE's JOBEX program with generalized internal coordinates and the corresponding STATPT module [16]. The ground state and the lowest singlet excited-state geometries of the carbazole-based oligomers were optimized by DFT and TDDFT, respectively, using the B3LYP [17–21] functional for the carbazole homopolymer (Cz-co-Cz)$_N$, the carbazole-co-fluorene (Cz-co-Fl)$_N$ and the carbazole-co-thiophene (Cz-co-Th)$_N$ oligomers (Fig. 1). The default m^3 numerical quadrature grid [22] was employed in all DFT calculations. The geometries of carbazole-based analogs were optimized without symmetry constraints using redundant internal coordinates and were considered converged if the gradient was less than 10^{-4} au. In all optimizations, the criterion for convergence was set to 10^{-8} for the energy and 10^{-7} for the density. To calculate excitation energies and analytic excited-state gradients, the TD-DFT method was used. Modules DSCF [22], GRAD, and ESCF [23] have been used. Sufficiently converged results were obtained with the valence-double-zeta quality with polarization functions SVP basis sets in close agreement with many previous studies; the conclusions are thus not expected to vary upon further basis set extensions [11–13]. In order to consider solvent effects on excitation energies, we adopted the conductor-like screening model (COSMO) [24] with a dielectric constant of $\varepsilon = 4.8$ to simulate the chloroform solvent and optimized atomic radii (C, 2.00 Å; N, 1.83 Å; O, 1.72 Å; H, 1.30 Å) for the construction of the molecular cavity were used for the calculations of all molecules.

For each oligomer in Fig. 1, the chain lengths studied varied from dimers to tetramers ($N = 1$, 2, 3 and 4). The first five singlet–singlet electronic transitions ($S_0 \rightarrow S_n$) were calculated for (Cz-co-Cz)$_N$, (Cz-co-Fl)$_N$, and (Cz-co-Th)$_N$ oligomers using the B3LYP/SVP and TD-B3LYP/SVP methods, respectively. Based on the optimized geometries of the oligomers, the electronic absorption and fluorescence spectra were calculated at the DFT and TD-DFT levels. The absorption and fluorescence excitation energies were obtained from the ground state and the

Table 1 Bond torsional angles of oligomers in ground (S_0) and lowest excited state (S_1) (in brackets) for the (Cz-co-Cz)$_N$, (Cz-co-Fl)$_N$ and (Cz-co-Th)$_N$ molecules optimized using B3LYP/SVP and TD-B3LYP/SVP (in parenthesis) methods



Oligomers	Bond torsional angles (°)						
	α	β	χ	δ	ϕ	γ	η
(Cz-co-Cz)$_N$							
$N = 1$	140.51						
	(170.24)						
$N = 2$	141.54	141.15	141.56				
	(155.15)	*(163.88)*	*(155.03)*				
$N = 3$	141.94	142.79	142.80	142.76	142.00		
	(147.13)	*(155.54)*	*(160.24)*	*(155.39)*	*(146.68)*		
$N = 4$	141.99	141.58	142.25	143.44	141.88	141.77	141.91
	(146.06)	*(152.82)*	*(159.91)*	*(154.50)*	*(155.69)*	*(148.60)*	*(143.88)*
(Cz-co-Fl)$_N$							
$N = 1$	142.14						
	(170.71)						
$N = 2$	142.20	142.19	142.30				
	(156.46)	*(167.58)*	*(155.39)*				
$N = 3$	142.53	143.38	142.40	143.21	142.42		
	(146.86)	*(157.03)*	*(164.52)*	*(157.34)*	*(148.24)*		
$N = 4$	142.69	142.60	142.44	141.78	142.66	142.59	143.04
	(156.46)	*(167.58)*	*(155.39)*	*(167.58)*	*(156.46)*	*(167.58)*	*(155.39)*
(Cz-co-Th)$_N$							
$N = 1$	21.06						
	(0.01)						
$N = 2$	27.23	27.41	27.00				
	(0.02)	*(0.00)*	*(0.00)*				
$N = 3$	24.19	24.52	25.67	24.72	25.61		
	(0.02)	*(0.04)*	*(0.02)*	*(0.00)*	*(0.03)*		
$N = 4$	26.82	25.78	27.81	26.14	27.53	25.49	26.04
	(0.00)	*(0.01)*	*(0.01)*	*(0.00)*	*(0.01)*	*(0.00)*	*(0.02)*

All torsional angles are given in degrees. *N* represents the number of the oligomer units

lowest singlet excited-state optimized geometries. The fluorescence electronic transitions were calculated as the vertical de-excitation based on the optimized geometry of the lowest excited state.

3 Results and discussion

3.1 Ground and excited states structural properties

The chain length dependence on the oligomer torsional angles (θ), both at ground and excited state has been investigated for the carbazole-based oligomers using our ground state optimized geometries. The torsion angles of the oligomers are given in Table 1 for the ground (S_0) and the lowest excited state (S_1) for the (Cz-co-Cz)$_N$, (Cz-co-Fl)$_N$ and (Cz-co-Th)$_N$ molecules.

The optimized structures of carbazole-based oligomers in the ground states are generally more distorted than the structures in excited states. We found twisted conformations with torsional angles (α, β, χ, δ, ϕ, γ and η) around 140° for both Cz-co-Cz-co-Cz and Cz-co-Fl-co-Cz. For Cz-co-Th-co-Cz, the torsional angles are around 30°, which means that the *syn* or *cis* structure of the copolymerized

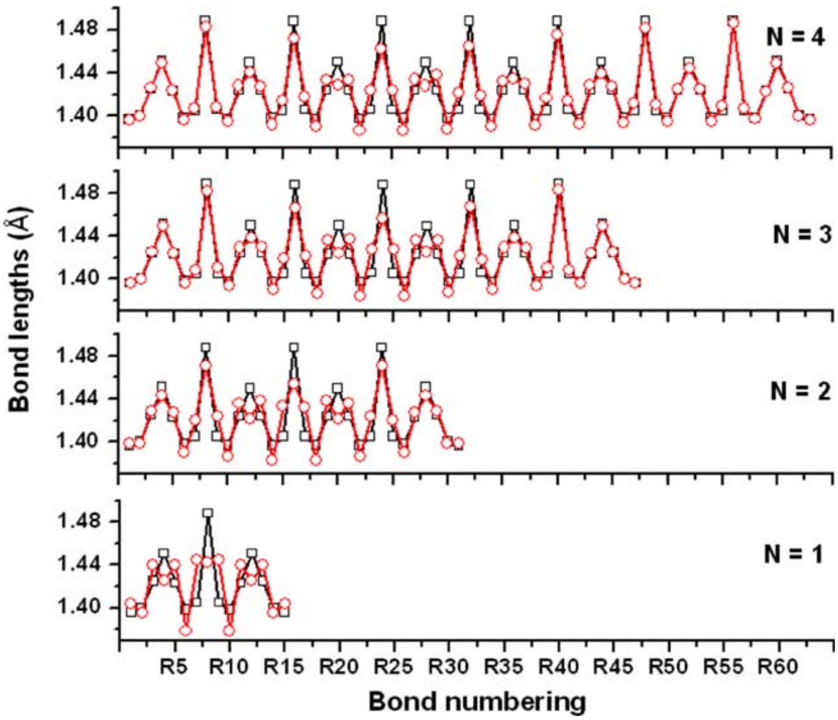


Fig. 2 Computed bond lengths of ground state and excited state of homocarbazole oligomers (Cz-co-Cz)$_N$. The *open square* denote electronic ground state and the *open circle* indicate the first excited state. Calculated at the B3LYP/SVP level of theory

heterocycles ring (thiophene) is energetically more favorable than the "trans" conformations [11, 12].

These ground state torsional angles appear independent the number of oligmer subunits used in the calculations. Only in the case of (Cz-co-Th)$_N$ is the monomer more planar than the oligomers. On the contrary, the excited state-torsion angles are more planar than the ground state geometries with torsional angles around 180° or 0°, respectively. The differences in the bond torsional angles between the ground and lowest singlet excited state can be explained by considering the bond length changes. The structures of the ground state and the lowest singlet excited-state optimized oligomers geometries are given in Figs. 2 and 3, where the changes bond lengths for copolymer derivatives and carbazole-based oligomer can be compared. The bond numbering schemes of (Cz-co-Cz)$_N$, (Cz-co-Fl)$_N$ and (Cz-co-Th)$_N$ oligomers are depicted in Fig. 1. In Fig. 2, the conjugated carbon–carbon bonds are illustrated for the ground state (S_0) and singlet excitations (S_1) for (Cz-co-Cz)$_N$ oligomers, dimer to octamer.

From Fig. 2, it is found that the carbon–carbon bonds which lie parallel to the polymer chain (i.e. bond numbering *R2*, *R4*, *R6, R8*, *R10*, *R12* and *R14*) become shorter while those that lie at angles other than 180° become longer. The carbon–carbon bonds are found to alternate in length between a single and double bond. In the lowest excited states, the double bond lengths increase, whereas the single bond length decreases with the changes being localized toward the centre of the oligomers. For example, the geometric changes in (Cz-co-Cz)$_{1,}$ (Cz-co-Cz)$_2$, (Cz-co-Cz)$_3$ and (Cz-co-Cz)$_4$ due to excitation affect the central units only. It should be noted that the spatial extent of the geometry deformations is not constant; the deformations continue to extend over the entire chain when the length increases, at least up to (Cz-co-Cz)$_{N=4}$ and this can be understood in terms of the degree of charge delocalization. For longer chains, the amount of charge per monomer unit is lower and thus the geometry change is smaller. The geometry change, as obtained from DFT calculations, are found in all the (Cz-co-Cz)$_N$ oligomer chains. This suggests that the center rings in the larger carbazole-based oligomers have more quinoidic character than the terminal rings [12, 13]. Therefore, the central rings in the larger oligomers were selected to confirm the trends of the C–C bond alternation along the backbone of the (Cz-co-Cz)$_3$, (Cz-co-Fl)$_3$ and (Cz-co-Th)$_3$ as shown in Fig. 3. We monitor the changes in bond length of these aromatic systems using the bond length alternation (BLA) [25]. The BLA values for selected molecular fragment can be defined as the differences in lengths between single bonds (d_{single}) and double bonds (d_{double}) of carbon–carbon atoms (Eq. 1). A positive BLA value indicates that the molecular unit has an aromatic (quinoidic) character [26–28].

$$BLA = \sum \frac{(d_{\text{single}} - d_{\text{double}})}{N}, \qquad (1)$$

The BLA associated with the carbon–carbon conjugated bond for the ground and singlet excitations states for the central rings of (Cz-co-Cz)$_3$, (Cz-co-Fl)$_3$ and (Cz-co-Th)$_3$ oligomer was estimated. We find that the BLA changes

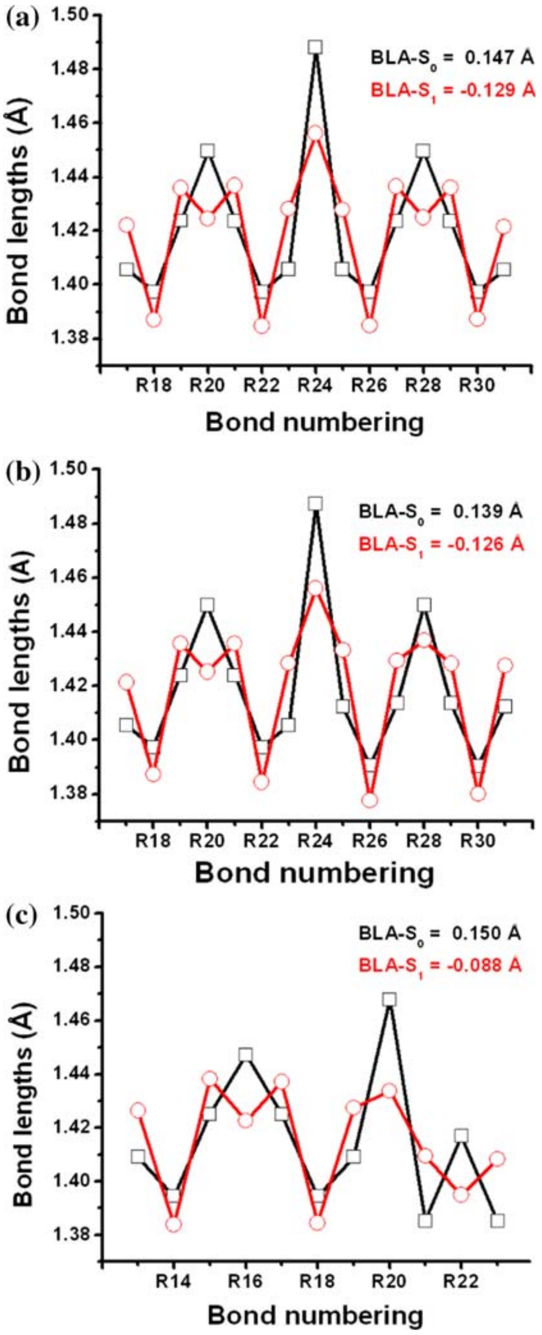


Fig. 3 The bond length alternating (BLA) of the central rings of the oligomers of (**a**) (Cz-co-Cz)$_3$, (**b**) (Cz-co-Fl)$_3$ and (**c**) (Cz-co-Th)$_3$ as shown. The open square denote electronic ground state and the open circle indicate the first excited state. Calculated using TD-DFT at the B3LYP/SVP level of theory

significantly in the excited states compared to the ground states, in the case of (Cz-co-Cz)$_3$ and (Cz-co-Fl)$_3$, decreasing from 0.147, 0.139 Å in S_0 to −0.129, −0.125 Å in S_1, respectively. In both, the ground and singlet states, the BLA differences are between 0.014 and 0.019 Å, whereas in the case of (Cz-co-Th)$_3$, the BLA decreases from 0.150 Å in S_0 to −0.088 Å in S_1. These results indicate that the thiophene unit leads to a decrease in the BLA value by 0.063 Å with respect to the (Cz-co-Cz)$_3$ and (Cz-co-Fl)$_3$ oligomers. In addition, the center of the quinoidic structures is located at the linking bonds between the copolymer units such as *R8*, as seen clearly in Fig. 1. Chidthong et al. [29] and Wichanee et al. [13] suggest that the elongation of the molecular chain leads to minor changes in the inter-ring distances of oligomers, the largest change localized at the terminal ring. In addition to, it was found that the inter-ring bond distances do not display appreciable variations with the oligomer size. Moreover, the bond-changing pattern is varied systematically when the molecular chain is elongated. These behaviors have been also found in the case of carbazole-based homopolymer and copolymer oligomers.

3.2 Absorption and fluorescence transitions

The absorption and fluorescence excitation energies calculated by the TD-B3LYP/SVP method are reported in Table 2. The excitations energies with highest oscillator strength (π–π^* transition) of each polymer calculated by TD-B3LYP/SVP method and were extrapolated by linear regression. There is a good linear relation ($r^2 = 0.99$) between the lowest excitations and the inverse chain length. A comparison the extrapolated energy of the absorption and fluorescence excitation with the experimental results and other computed values is shown in Table 2. From these results, it was found that the excitation energies of these materials are lower than the experimental data, 0.34, 0.31, and 0.18 eV (absorption) and 0.33, 0.51, and 0.69 eV (fluorescence) for its carbazole-based, (Cz-co-Cz)$_N$, (Cz-co-Fl)$_N$ and (Cz-co-Th)$_N$, respectively. Cornil et al. [30, 31] have shown that this can result from the overestimation of long-range electron correlation effects in the TD-DFT methods. Previous works [30–33] have shown that the high accuracy of DFT functionals such as TPSS functional is more suitable for calculation of conjugated oligomers. However, for small molecules, the impact of inductive and/or mesomeric effects induced by substituents appears to be well reproduced; however, the agreement with the correspondingly experimental values deteriorates when the chain size is increased. Our results confirm previous reports that a proper extrapolation procedure recommends the use of a rather large number of oligomers to improve the accuracy of the fit, and an accurate fitting function [30, 31, 34–37]. In fact, in order to obtain more accurate excitation energy for an infinite oligomer, one needs to use higher order polynomials. Jansson et al. studied the chain length dependence of singlet and triplet excited states of oligofluorene and used an empirical relationship proposed by Meier et al. [35, 36]. They discussed in detail the concept of “effective conjugation length”

Table 2 The calculation absorption (E_{abs}), fluorescence energies (E_{flu}) and fluorescence lifetimes of carbazole-based polymers

Oligomers	Absorption	Fluorescence	
	E_{abs} (eV)	E_{flu} (eV)	Lifetime (ns)
(Cz-co-Cz)$_N$			
$N = 1.0$	3.84	3.28 (1.484)	1.44
$N = 1.5$	3.51	2.91 (2.482)	1.10
$N = 2.0$	3.36	2.83 (3.222)	0.89
$N = 2.5$	3.26	2.77 (3.933)	0.76
$N = 3.0$	3.21	2.76 (4.561)	0.66
$N = 4.0$	3.17	2.76 (5.814)	0.52
$N = \infty$	2.91	2.51	
Expt.	3.25[a]	2.84[a]	
(Cz-co-Fl)$_N$			
$N = 1.0$	3.80	3.23 (1.517)	1.46
$N = 2.0$	3.32	2.77 (3.242)	0.93
$N = 3.0$	3.18	2.68 (4.537)	0.71
$N = 4.0$	3.14	2.63 (7.076)	0.47
$N = \infty$	2.89	2.40	
Expt.	3.20[a]	2.91[a]	
(Cz-co-Th)$_N$			
$N = 1.0$	3.87	3.59 (0.862)	2.07
$N = 2.0$	3.14	2.57 (2.318)	1.50
$N = 3.0$	2.87	2.34 (3.517)	1.20
$N = 4.0$	2.81	2.25 (4.598)	0.99
$N = \infty$	2.42	1.74	
Expt.	2.60[b]	2.43[b]	

Values in parentheses are oscillator strengths

[a] Ref. [6]

[b] Ref. [7]

(ECL), defined as the conjugation length at which the wavelength of the absorption maximum in the series of oligomers is not more than 1 nm above the lower limit, which is given by the infinitely long polymer chain [30, 35–37]. From this definition, the ECL largely differs for the various oligomer series. Given these issues, we focus on ECL for estimate the excitation energies of these systems in the following section.

We estimate the ECL for all selected oligomers based on the convergence of the calculated excited energies of the first dipole-allowed excited states with the increasing chain length (Fig. 4). The ECL was estimated by the convergence of excitation energies with the chain length within a threshold of 0.05 eV, based on the obtained linearity between the excitation energy and reciprocal chain length. Apart from the selected carbazole-based oligomers, well-studied oligomers, such as (Cz-co-Cz)$_N$, (Cz-co-Fl)$_N$ and (Cz-co-Th)$_N$ oligomers are also reexamined with TDDFT for further validating the theory and for comparison. These results will be discussed only briefly.

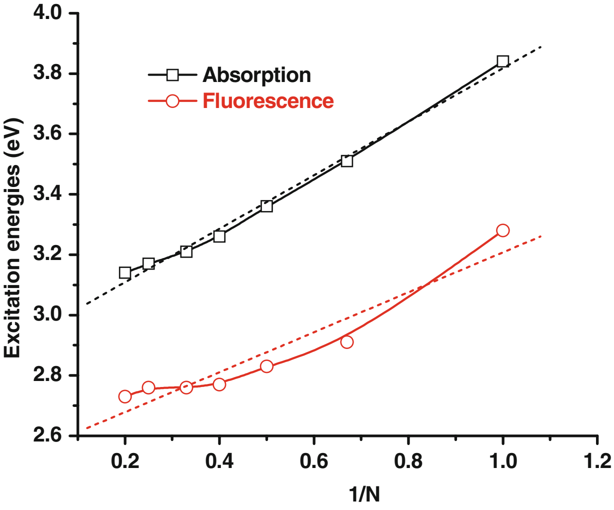


Fig. 4 First singlet excitation energies as calculated by TDDFT for absorption and fluorescence energies in poly(2,7-carbazole) oligomers, as a function of 1/*N*

We present their absorption and fluorescence energies in Table 2 by applying the ECLs for the absorption and fluorescence energies for compounds (Cz-co-Cz)$_N$, (Cz-co-Fl)$_N$ and (Cz-co-Th)$_N$ oligomers. The ECL value at which a convergence of the optical properties, absorption and emission properties is reached corresponds to $N = 4$ for (Cz-co-Cz)$_N$, (Cz-co-Fl)$_N$ and (Cz-co-Th)$_N$ oligomers. Comparison of the results between experiment and absorption spectrum calculations of are shown in Fig. 5 and indicate that the estimated excitation energies, at ECLs $N = 4$, are in good agreement with the optical properties. We therefore conclude that this procedure can be used to reliably estimate the excitation energies of such polymers.

We next look at the details of the electronic transitions of each carbazole-based tetramer ($N = 4$) at TD-B3LYP/SVP level (Table 3) which can be used to describe the possible excitations of all carbazole-based molecules. From the absorption transitions, it was found that for (Cz-co-Cz)$_4$, (Cz-co-Fl)$_4$ and (Cz-co-Th)$_4$ molecules, the $S_0 \rightarrow S_1$ excitation primarily corresponds to the promotion of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) (H → L) (in Fig. 6) as indicated by large oscillator strengths (*f*) of : 6.112, 6.169 and 4.277, respectively. The isosurface plot of the HOMO and LUMO (Fig. 6) indicate an exchange of the double and single bonds as is typical for a $\pi \rightarrow \pi^*$ transition in conjugated polymers. On the other hand, the S_2, S_3 and S_4 electronic transitions of each compound possess very small oscillator strengths. The fluorescence energies and the radiative lifetimes of (Cz-co-Cz)$_4$, (Cz-co-Fl)$_4$ and (Cz-co-Th)$_4$ computed with the TD-B3LYP/SVP method using S_1 state optimized geometries are collected in Table 3. The fluorescence energies were

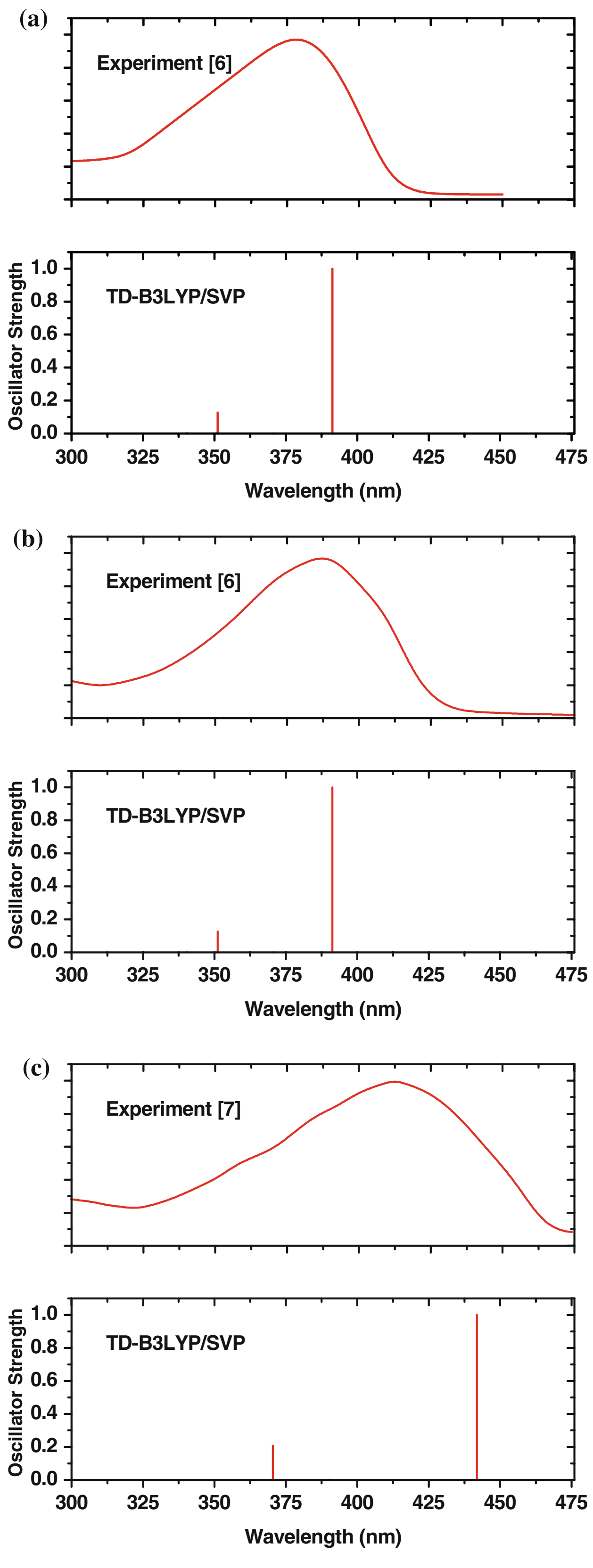


Fig. 5 Absorption spectra [6, 7] and TD-B3LYP/SVP calculations of (Cz-co-Cz)$_4$, (Cz-co-Fl)$_4$ and (Cz-co-Th)$_4$ oligomers

also investigated. From Table 2, it is clear that the fluorescence energies of (Cz-co-Th)$_N$ and (Cz-co-Fl)$_N$ molecules are red-shifted from the excitation energies of (Cz-co-Cz)$_N$ with values of 2.76, 2.63 and 2.25 eV for (Cz-co-Cz)$_N$, (Cz-co-Fl)$_N$ and (Cz-co-Th)$_N$, respectively. These energies are in good agreement with experimental values [6, 7].

The differences in absorption and fluorescence energies should also lead to different Stokes shifts. We therefore evaluate the Stokes-shift as the differences $\Delta E = E_{\mathrm{abs}} - E_{\mathrm{flu}}$. The TD-B3LYP/SVP values exhibit Stokes shift of about 0.3 eV for (Cz-co-Fl)$_N$ and are lower than those for (Cz-co-Cz)$_N$ and (Cz-co-Th)$_N$ by about 0.6 eV. This result demonstrates that the (Cz-co-Fl)$_N$ structure is more relaxed than those of (Cz-co-Cz)$_N$ and (Cz-co-Th)$_N$ upon excitation. These results also show that the electronic excitation leads to the formation of a quinoide-type structure.

Using the computed structures, we can also relate the differences in the bond lengths between the ground (GS) and lowest singlet excited state (ES) to the molecular orbital nodal patterns. Because the lowest singlet state corresponds to an excitation from the HOMO to the LUMO in all of the oligomers considered here (Fig. 5), the bond-length variations were explored further in terms of the changes to the HOMO and LUMO. By comparing Fig. 5, we can see that the HOMO has nodes across the *R1, R3, R5, R7, R9, R11* and *R13* bonds in all molecules, but the LUMO is bonding in these regions. Therefore, one would expect a contraction of these bonds. The data reported in Fig. 2 and Fig. 3 do in fact show this given the bonds are in fact considerably shorter in the excited state. However, the bond length will increase when the bonding changes to antibonding. The dihedral angle (Table 1) between the two adjacent units shortened from 140° to 170° in (Cz-co-Cz)$_N$ and (Cz-co-Fl)$_N$ molecules. Whereas the dihedral angle of (Cz-co-Th)$_N$ shortened from 28° to nearly 0°. It is obvious that the excited structure has a strong coplanar tendency in all molecules. It is indicated that is, the conjugation is better in the excited structure. In this result, it can see that geometry of excited state is more planar than ground state.

Finally, to investigate the effects of the structural relaxation upon excitation, radiative lifetimes were investigated. Based on the fluorescence energy and oscillator strength, the radiative lifetimes have been computed for spontaneous emission using the Einstein transition probabilities according to the formula (in au) [29, 38, 39].

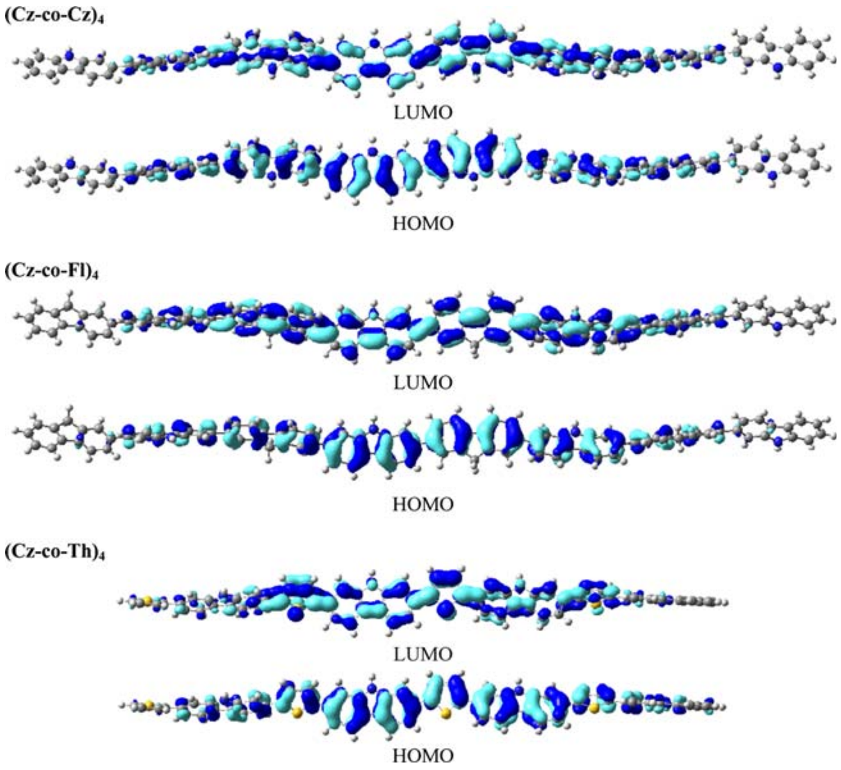
$$\tau = \frac{c^3}{2(E_{\mathrm{Flu}})^2 f} \qquad (2)$$

In Eq. 2, c is the velocity of light, E_{Flu} is the transition energy and f is the oscillator strength. The computed lifetimes, τ, for the carbazole-based oligomers are depicted

Table 3 Excitation energies (E_{ex}(eV)), oscillator strengths (*f*), and wave function compositions for the lowest singlet electronic states of (Cz-co-Cz)$_4$, (Cz-co-Fl)$_4$ and (Cz-co-Th)$_4$ molecules computed by TD-B3LYP/SVP

Electronic transitions	E_{ex}	*f*	Wave function composition
(Cz-co-Cz)$_4$			
Absorption			
$S_0 \rightarrow S_1$	3.17	6.112	H → L(61.8%), H-1 → L+1(25.1%)
$S_0 \rightarrow S_2$	3.34	0.002	H-1 → L(45.8%), H → L+1(45.8%)
$S_0 \rightarrow S_3$	3.51	0.773	H-1 → L+1(46.5%), H → L+2(31.8%)
$S_0 \rightarrow S_4$	3.54	0.008	H-1 → L+1(47.4%), H → L+1(46.8%)
Fluorescence			
$S_1 \rightarrow S_0$	2.76	5.814	H → L(65.3%), H-1 → L+1(17.8%)
(Cz-co-Fl)$_4$			
Absorption			
$S_0 \rightarrow S_1$	3.14	6.169	H → L(61.4%), H-1 → L+1(25.8%)
$S_0 \rightarrow S_2$	3.31	0.011	H-1 → L(46.4%), H → L+1(45.4%)
$S_0 \rightarrow S_3$	3.50	0.039	H → L+1(46.9%), H-1 → L(46.3%)
$S_0 \rightarrow S_4$	3.51	0.731	H → L+1(47.1%), H-2 → L(30.6%)
Fluorescence			
$S_1 \rightarrow S_0$	2.63	7.076	H → L(59.9%), H + 1→L + 1(28.7%)
(Cz-co-Th)$_4$			
Absorption			
$S_0 \rightarrow S_1$	2.81	4.277	H → L(65.0%), H-1 → L+1(18.4%)
$S_0 \rightarrow S_2$	3.10	0.000	H → L+1(47.9%), H-1 → L (45.3%)
$S_0 \rightarrow S_3$	3.18	0.012	H-1 → L+1(50.0%), H → L+1(47.0%)
$S_3 \rightarrow S_4$	3.35	0.886	H-1 → L+1(63.3%), H → L (19.1%)
Fluorescence			
$S_1 \rightarrow S_0$	2.25	4.598	H → L(65.7%), H-1 → L+1(13.3%)

Fig. 6 HOMO and LUMO of (Cz-co-Cz)$_4$, (Cz-co-Fl)$_4$ and (Cz-co-Th)$_4$ oligomers. Depicted are two isosurfaces of equal values but opposite sign



in Table 2. The lifetime of carbazole-based oligomers at $N = 4$ amounts to 0.52, 0.47, and 0.99 ns for (Cz-co-Cz)$_N$, (Cz-co-Fl)$_N$ and (Cz-co-Th)$_N$, respectively. Among the carbazole-based molecules, the (Cz-co-Fl)$_N$ shows the lowest lifetime, which is close to that of (Cz-co-Cz)$_N$. For the purpose of comparison, the results of a chemically similar system were used. The radiative lifetimes of poly(*N*-octyl-2,7-carbazole) and poly(*N*-octyl-2,7-carbazole-alt-9,9-dioctyl-2,7-fluorene) in THF solution are 0.51 and 0.45 ns [28] which is in good agreement with the predicted lifetimes of (Cz-co-Cz)$_N$ (0.52 ns) and (Cz-co-Fl)$_N$ (0.47 ns), respectively. Similar results have been reported for several other polymers (thin films) [40–44] and it can be concluded that their low radiative lifetime can produce useful fluorescent emission [40–44].

4 Conclusions

Absorption and fluorescence properties of (Cz-co-Cz)$_N$, (Cz-co-Fl)$_N$ and (Cz-co-Th)$_N$, are presented herein. The optimized ground state and the first singlet excited electronic state have been obtained using B3LYP and TD-B3LYP, methods, respectively, in conjunction with the SVP basis set. A chloroform solvent effect on excitation has been assessed using the COSMO implicit solvent model.

The estimated excitation energies of the absorption and fluorescence excitation based on ECLs $N = 4$ are in good agreement with the optical properties of (Cz-co-Cz)$_N$, (Cz-co-Fl)$_N$ and (Cz-co-Th)$_N$ polymers, 3.17, 3.14 and 2.81 eV (absorption) and 2.76, 2.63 and 2.25 eV (fluorescence), respectively. Compared to experimental fluorescence excitation energies available for (Cz-co-Cz)$_N$, (Cz-co-Fl)$_N$ and (Cz-co-Th)$_N$, it can be seen that TD-B3LYP/SVP calculations give good predictions of the excitation energies for the S_1 transition (2.84, 2.91 and 2.43 eV, respectively). This suggests that the procedure used herein is reliable method for the estimation of excitation energies of such polymers.

Moreover, we find that the geometry of excited states is more planar than that of the ground states. The excitation to the S_1 state causes significant changes in the predicted geometry which is in agreement with the small Stokes shifts observed experimentally. Furthermore, the radiative lifetime of carbazole-based oligomers at $N = 4$ amounts to 0.52, 0.47 and 0.99 ns for (Cz-co-Cz)$_N$, (Cz-co-Fl)$_N$ and (Cz-co-Th)$_N$, respectively, which is in agreement with the experiment lifetimes of (Cz-co-Cz)$_N$ (0.51 ns) and (Cz-co-Fl)$_N$ (0.45 ns), respectively. It is shown that the existence of multi-components in the fluorescence decay profiles of polymers is caused by several distinct intermolecular π–π* interactions. We therefore conclude that homopolymers and copolymers derived from *N*-substituted-2,7-carbazoles appear to be very promising materials for the future development of light-emitting diodes, electrochromic windows, photovoltaic cells, photorefractive materials.

Acknowledgments Supporting from the Thailand Research Fund (RTA5080005 to SH and MRG5180287 to SS), and the National Center of Excellence in Petroleum, Petrochemical Technology, Center of Nanotechnology Kasetsart University, Kasetsart University Research and Development Institute (KURDI), National Nanotechnology Center (NANOTEC) and Laboratory of Computational and Applied Chemistry (LCAC) are gratefully acknowledged. The calculations were performed in part on the Schrödinger III cluster of the University of Vienna. Thanks are also due to Matthew Paul Gleeson for helpful comments and reading of the manuscript.

References

1. Burroughes JH, Bradley DDC, Brown AR, Marks RN, Friend RH, Burn PL, Holmes AB (1990) Light-emitting diodes based on conjugated polymers. Nature 347:339–341
2. Morin JF, Beaupre S, Leclerc M, Levesque I, D'Iorio M (2002) Blue light-emitting devices from new conjugated poly(*N*-substituted-2,7-carbazole) derivatives. Appl Phys Lett 80(3):341–343
3. Morin JF, Leclerc M (2001) Syntheses of conjugated polymers derived from *N*-alkyl-2,7-carbazoles. Macromolecules 34(14): 4680–4682
4. Zotti G, Schiavon G, Zecchin S, Morin JF, Leclerc M (2002) Electrochemical, conductive, and magnetic properties of 2,7-carbazole-based conjugated polymers. Macromolecules 35(6): 2122–2128
5. Morin JF, Boudreault PL, Leclerc M (2003) Blue-light-emitting conjugated polymers derived from 2,7-carbazoles. Macromol Rapid Commun 23:1032–1036
6. Bouchard J, Belletete M, Durocher G, Leclerc M (2003) Solvatochromic properties of 2,7-carbazole-based conjugated polymers. Macromolecules 36:4624–4630
7. Morin JF, Leclerc M (2002) 2,7-Carbazole-based conjugated polymers for blue, green, and red light emission. Macromolecules 35(22):8413–8417
8. Belletete M, Bedard M, Leclerc M, Durocher G (2004) Absorption and emission properties of carbazole-based dyads studied from experimental and theoretical investigations. Synth Met 146(1):99–108
9. Belletete M, Bedard M, Leclerc M, Durocher G (2004) Ground and excited state properties of carbazole-based dyads: correlation with their respective absorption and fluorescence spectra. J Mol Struct (THEOCHEM) 679(1–2):9–15
10. Belletete M, Bedard M, Bouchard J, Leclerc M, Durocher G (2004) Spectroscopic and photophysical properties of carbazole-based triads. J Can J Chem 82:1280–1288
11. Suramitr S, Hannongbua S, Wolschann P (2007) Conformational analysis and electronic transition of carbazole-based oligomers as explained by density functional theory. J Mol Struct (THEOCHEM) 807(1–3):109–119
12. Marcon V, Van der Vegt N, Wegner G, Raos G (2006) Modeling of molecular packing and conformation in oligofluorenes. J Phys Chem B 110(11):5253–5261
13. Meeto W, Suramitr S, Vannarat S, Hannongbua S (2008) Structural and electronic properties of poly(fluorine-vinylene) copolymer and its derivatives: Time-dependent density functional theory investigation. Chem Phys 349(1–3):1–8
14. Jespersen KG, Beenken WJD, Zaushitsyn Y, Yartsev A, Andersson M, Pullerits T, Sundström V (2004) The electronic states

of polyfluorene copolymers with alternating donor–acceptor units. J Chem Phys 121:12613–12617

15. Ahlrichs R, Bär M, Häser M, Horn H, Kölmel C (1989) Electronic structure calculations on workstation computers: the program system turbomole. Chem Phys Lett 162(3):165–169
16. von Arnim M, Ahlrichs R (1999) Geometry optimization in generalized natural internal coordinates. J Chem Phys 111(20): 9183–9190
17. Dirac PAM (1929) Quantum mechanics of many-electron systems. Proc R Soc Lond A 123:714–733
18. Slater JC (1951) A simplification of the Hartree–Fock method. Phys Rev 81:385–390
19. Vosko SH, Wilk L, Nusair M (1980) Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. Can J Phys 58(8):1200–1211
20. Becke AD (1988) Density-functional exchange-energy approximation with correct asymptotic behavior. Phys Rev A 38(6): 3098–3100
21. Kohn W, Becke AD, Parr RG (1996) Density functional theory of electronic structure. J Chem 100(31):12974–12980
22. Treutler O, Ahlrichs R (1995) Efficient molecular numerical integration schemes. J Chem Phys 102(1):346–354
23. Bauernschmitt R, Ahlrichs R (1996) Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory. Chem Phys Lett 256(4–5):454–464
24. Klamt A, Schüürmann G (1993) COSMO: a new approach to dielectric screening in solvents with explicit expressions for the screening energy and its gradient. J Chem Soc Perkin Trans 2:799–805
25. Jacquemin D, Perpete EA, Chermette H, Ciofini I, Adamo C (2007) Comparison of theoretical approaches for computing the bond length alternation of polymethineimine. Chem Phys 332(1): 79–85
26. Liu Q, Liu W, Yao B, Tian H, Xie Z, Geng Y, Wang F (2007) Synthesis and chain-length dependent properties of monodisperse oligo(9, 9-di-n-octylfluorene-2,7-vinylene)s. Macromolecules 40(6):1851–1857
27. Yang L, Ren AM, Feng JK, Wang JF (2005) Theoretical investigation of optical and electronic property modulations of pi-conjugated polymers based on the electron-rich 3, 6-dimethoxy-fluorene unit. J Org Chem 70(8):3009–3020
28. Wang JF, Feng JK, Ren AM, Liu XD, Ma YG, Lu P, Zhang HX (2004) Theoretical studies of the absorption and emission properties of the fluorene-based conjugated polymers. Macromolecules 37(9):3451–3458
29. Chidthong R, Hannongbua S, Aquino A, Wolschann P, Lischka H (2007) Excited state properties, fluorescence energies, and lifetime of a poly(fluorene-pyridine) copolymer, based on TD-DFT investigation. J Comput Chem 28(10):1735–1742
30. Cornil J, Gueli I, Dkhissi A, Sancho-Garcia JC, Hennebicq E, Calbert JP, Lemaur V, Beljonne D (2003) Electronic and optical properties of polyfluorene and fluorene-based copolymers: a quantum-chemical characterization. J Chem Phys 118:6615–6623
31. Gierschner J, Cornil J, Egelhaaf HJ (2007) Optical bandgaps of π-conjugated organic materials at the polymer limit: experiment and theory. Adv Mater 19:173–191
32. Sancho-García JC (2006) Assessing a new nonempirical density functional: difficulties in treating π-conjugation effects. J Chem Phys 124:124112/1–124112/10
33. Sancho-García JC (2007) Treatment of singlet–triplet splitting of a set of phenylene ethylenes organic molecules by TD-DFT. Chem Phys Lett 439:236–242
34. Jansson E, Chandra Jha P, Ågren H (2007) Chain length dependence of singlet and triplet excited states of oligofluorenes: a density functional study. Chem Phys 336(2–3):91–98
35. Meier H, Stalmach U, Kolshorn H (1997) Effective conjugation length and UV/vis spectra of oligomers. Acta Polymer 48:379–384
36. Oelkrug D, Tompert A, Egelhaaf HJ, Hanack M, Steinhuber E, Hohloch M, Meier H, Stalmach U (1996) Towards highly luminescent phenylene vinylene films. Synth Met 83(3):231–237
37. Peach GMJ, Tellgren EI, Saek P, Helgaker T, Tozer DJ (2007) Structural and electronic properties of polyacetylene and polyyne from hybrid and coulomb-attenuated density functionals. J Phys Chem A 111(46):11930–11935
38. Luke V, Aquino A, Lischka H, Kauffmann HF (2007) Dependence of optical properties of oligo-*para*-phenylenes on torsional modes and chain length. J Phys Chem B 111(28):7954–7962
39. Beenken WJD, Lischka H (2005) Spectral broadening and diffusion by torsional motion in biphenyl. J Chem Phys 123: 144311–144319
40. Tirapattur S, Belletete M, Drolet N, Leclerc M, Durocher G (2003) Steady-state and time-resolved studies of 2,7-carbazole-based conjugated polymers in solution and as thin films: determination of their solid state fluorescence quantum efficiencies. Chem Phys Lett 370(5–6):799–804
41. Jenekhe SA, Lu L, Alam MM (2001) New conjugated polymers with donor–acceptor architectures: Synthesis and photophysics of carbazole-quinoline and phenothiazine-quinoline copolymers and oligomers exhibiting large intramolecular charge transfer. Macromolecules 34(21):7315–7324
42. Schenning APH, Tsipis AC, Meskers SCJ, Beljonne D, Meijer EW, Brdas JL (2002) Electronic structure and optical properties of mixed phenylene vinylene/phenylene ethynylene conjugated oligomers. Chem Mater 14(3):1362–1368
43. Pålsson LO, Wang C, Russell DL, Monkman AP, Bryce MR, Rumbles G, Samuel DW (2002) Photophysics of a fluorene copolymer in solution and films. Chem Phys 279(2–3):229–237
44. Sun RG, Wang YZ, Wang DK, Zheng QB, Kyllo EM, Gustafson TL, Wang F, Epstein AJ (2000) High PL quantum efficiency of poly(phenylene vinylene) systems through exciton confinement. Synth Met 111–112:595–602