Effects of the CN and NH$_2$ substitutions on the geometrical and optical properties of model vinylfluorenes, based on DFT calculations

Wichanee Meeto [a], Songwut Suramitr [a], Vladimír Lukeš [b], Peter Wolschann [c], Supa Hannongbua [a,*]

[a] Department of Chemistry, Faculty of Science, and Center of Nanotechnology, Kasetsart University, Bangkok 10900, Thailand
[b] Department of Chemical Physics, Slovak University of Technology, Radlinského 9, SK-81 237 Bratislava, Slovakia
[c] Institute for Theoretical Chemistry, University of Vienna, Währingerstrasse 17, A-1090 Wien, Austria

ABSTRACT

A systematic study on the structural and photo-physical properties of model bifluorenevinylene compounds based on the density functional theory (DFT) and its time-dependent (TD-DFT) version is presented. The main aim of this work is to investigate the influence of substitution on bifluorenevinylene using strong electron acceptor CN or electron donor NH$_2$ groups on: (a) the optimal geometry, (b) torsional potentials and (c) photo-physical properties. Our results indicate that the substitution on the vinylene bridge, leads to the twisting of molecular fragment on the side of added group and are in good overall agreement with experiment. In the case of the amino mono-substituted bifluorenevinylene, the amino group leads to non-planarity at the non-substituted portion of the molecule. The chemical modification also have a pronounced impact on the electronic properties. The shape of the potential energy curves evaluated for the lowest vertically excited states is heavily dependent on the molecular conformation. Finally, we discuss how the structural and electronic information presented here can be useful in designing of novel optical materials as well as understanding of excitation–relaxation phenomena which may occur in various time-dependent optical experiments.

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1. Introduction

Polyfluorenes, with their excellent photoluminescence quantum characteristics, excellent solubility in common organic solvents, can be used as blue-shift emitters [1,2]. Additionally, their thermal and chemical stability can be modified and improved by adding of different alkyl substiuents at the 9-th position of the fluorene ring [3]. However, the polyfluorenes systems containing simple connected fluorene units tend to aggregate in the condensed phase and provide less effective performance. Fortunately, these problems can be limited with the modification of their molecular structure, such as the polyfluorene-2,7-vinylenes (PFVs) [4]. Moreover, the various electron-donating or electron-accepting groups can be added to the vinylene bridge located within the aromatic molecular chain which subtly alters the intermolecular steric interactions which can be used to effectively tune the optical spectra from blue to the infrared region without the necessity to perturb the planarity of aromatic units [5,6].
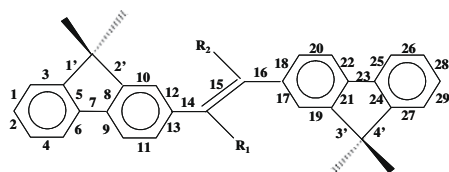
Theoretical quantum studies of π-conjugated oligomers or polymers can provide a fundamental understanding of the physical process occurring, and make a considerable contribution to the design of novel optoelectronic materials. These include theoretical studies done using semiempirical, *ab initio* and density functional theory (DFT) methods, focusing on the electronic properties based on the ground-state equilibrium geometries [7–10]. Among them, the DFT approach and its time-dependent (TD) extension [11] for the excited states have been successfully demonstrated in investigations of optical and electronic properties of moderate to large organic conjugated oligomers [12]. These results are often used in cooperation with the experimental data to characterize the structural, electronic and optical properties of conjugated polymers and represent primary information to aid in our understanding of phenomena connected with conformation relaxation processes occurring during the electronic excitation and/or de-excitation [13]. Bifluorenevinylene derivatives are the focus of this research investigation, being shortest computationally efficient representation of oligo- and poly-vinylfluorenes which are of significant scientific interest.

The main aim of this work is the investigation of the direct influence of substitution using strong electron acceptor CN or electron donor NH$_2$ groups on the optimal geometry, torsional potentials and photo-physical properties. We do this by modifying the electronic structure of these model systems by the symmetric or asymmetric addition of the representative electron-accepting cyano and electron-donating amino groups on vinyl positions (see Fig. 1). We focus on the *all-trans* conformations and the electronic ground-state torsional potential curves in this investigation. The

Molecule	R₁	R₂
F_2V	H	H
F_2V-$(CN)_2$	CN	CN
F_2V-$(NH_2)_2$	NH_2	NH_2
F_2V-CN	CN	H
F_2V-NH_2	NH_2	H
F_2V-CN-NH_2	CN	NH_2

Fig. 1. Schematic structure, bond and dihedral angle numbering of studied systems in *all-trans* conformation.

corresponding vertical excitation characteristics of these molecules are calculated using (TD-)DFT method. Finally, the physical origin of the lowest electronic transitions will be explained using molecular orbital analysis.

2. Methodology

The geometries and torsion potential of studied dimers F_2V, F_2V–$(CN)_2$, F_2V–$(NH_2)_2$, F_2V–CN, F_2V–NH_2 and F_2V–CN–NH_2 (formula and abbreviations are given in Fig. 1) are optimized by the DFT method using the Becke three parameter hybrid (B3LYP) [14] functional in conjunction with the 6-31G(d) basis set [15]. The torsion potentials were calculated for the fixed angles from the

Table 1
The B3LYP/6-31G(d) optimal dihedral angles (in deg) and BLA parameters (in Å) for *all-trans* conformations.

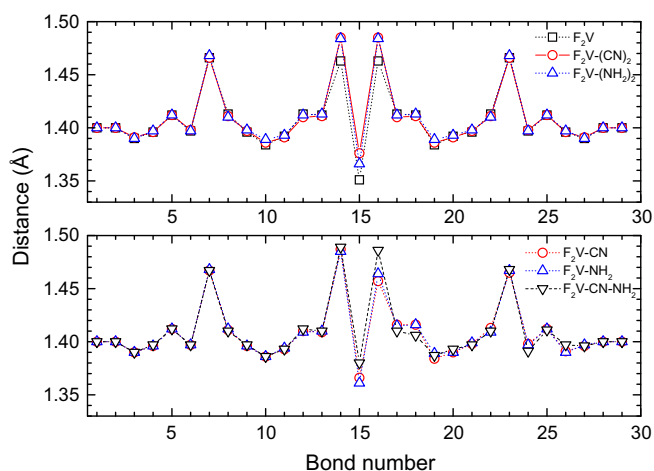| Molecule	Θ_1	Θ_2	BLA
F_2V	0	0	0.224
F_2V-$(CN)_2$	38	−38	0.218
F_2V-$(NH_2)_2$	45	−45	0.236
F_2V-CN	28	−7	0.212
F_2V-NH_2	36	−31	0.227
F_2V-CN-NH_2	52	−44	0.223

Fig. 2. Computed B3LYP/6-31G(d) bond lengths of the molecules under study in *all-trans* conformation. For notation see Fig. 1.

Table 2
The lowest excitation energies in eV and oscillator strengths (values in parentheses) for the optimal *all-trans* geometries. The values written in italics stand for the excitation contributions in percentage involved in each calculated transition (H denotes HOMO and L is LUMO).

Molecule	S_1	S_2	S_3	S_4	S_5	S_6	S_7
F_2V	3.23 (1.870)	3.98 (0.000)	4.18 (0.000)	4.19 (0.006)	4.41 (0.00)	4.44 (0.019)	4.44 (0.000)
	99%: H → L	60%: H−1 → L	50%: H → L+3	68%: H → L+2	43%: H → L+2	33%: H−2 → L	60%: H−3 → L
		38%: H → L+1					
F_2V-$(CN)_2$	2.82 (0.907)	3.22 (0.000)	3.64 (0.009)	3.67 (0.000)	3.67 (0.000)	3.88 (0.000)	4.29 (0.336)
	99%: H → L	97%: H−1 → L	70%: H−2 → L	75%: H−3 → L	68%: H−4 → L	73%: H−5 → L	72%: H−6 → L
F_2V-$(NH_2)_2$	2.90 (0.586)	3.30 (0.000)	3.53 (0.009)	3.61 (0.000)	4.21 (0.016)	4.24 (0.000)	4.41 (0.713)
	99%: H → L	97%: H → L+1	94%: H → L+2	92%: H → L+3	91%: H → L+4	90%: H → L+5	93%: H−2 → L+1
F_2V-CN	3.08 (1.424)	3.72 (0.096)	4.08 (0.002)	4.08 (0.016)	4.22 (0.007)	4.26 (0.006)	4.39 (0.063)
	99%: H → L	91%: H−1 → L	98%: H−2 → L	62%: H−3 → L	42%: H−5 → L	44%: H−4 → L	75%: H → L+1
F_2V-NH_2	3.29 (1.099)	3.86 (0.251)	4.03 (0.013)	4.08 (0.021)	4.40 (0.079)	4.54 (0.023)	4.58 (0.027)
	99%: H → L	87%: H → L+1	67%: H → L+2	69%: H → L+3	83%: H−1 → L	39%: H → L+6	41%: H → L+5
F_2V-CN-NH_2	3.53 (0.824)	4.01 (0.165)	4.25 (0.006)	4.29 (0.085)	4.38 (0.010)	4.41 (0.131)	4.63 (0.015)
	98%: H → L	73%: H → L+1	70%: H−1 → L	67%: H → L+1	61%: H → L+3	70%: H−2 → L	70%: H−4 → L