

Reactivity and structural study of all mono-, and di-fluorocarbazoles; a computational study

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Abstract: All mono-, and di-fluorocarbazoles and their radical cations have been studied using density functional theory at B3LYP/6-311+G, HF/6-311+G// B3LYP /6-311+G, and MP2/6-311+G// B3LYP /6-311+G levels of theory. The effects of the position of the fluorine atom on the properties of the carbazole molecule have been studied using optimized structures obtained for these molecules and their radical cations. Charge- and spin-density distribution, size and direction of dipole moment vector, ionization potential, electric polarizability of these molecules have been calculated and analyzed as well. The analysis of these data showed that double bonds in 1,6-difluorocarbazole are more delocalized and it is the best possible monomer among all molecules for electropolymerization.

Keywords: B3LYP/6-311+G; Carbazole; Ionization potential; Dipole moment.

Introduction

Conjugated polymers have been proposed for use in a wide variety of next generation technologies including displays, solid-state lighting, transistors and organic photovoltaic devices [1-3], but relatively little is known about how these polymers pack with the exception of a few materials [4]. The active layer in organic photovoltaic bulk heterojunction devices is composed of a blend of π -conjugated, electron-donor polymers and electron-acceptor molecules. Whereas the optoelectronic properties of the electron-donor polymer are primarily determined by the choice of the conjugated backbone, the solubility is predominantly determined by the position, length and makeup of the alkyl side chains.

Both the polymer backbone and the alkyl side chains influence device efficiency and molecular packing structure, especially in donor-acceptor copolymers, which contain an ordered sequence of different subunits [5-7]. Systematic studies of the effect of different side-chain groups, with the same backbone, have shown that the length and the type of alkyl chains affect the packing structure of the active layer, such as the π - π distance and polymer orientation, and these properties have been correlated with the device performances, fill factor, and open circuit voltage and short circuit current. Decreasing the length (volume) of the alkyl chains has the potential to improve the polymer's charge mobility and optical density because these regions are resistive and do not contribute to optical absorption, but steric and other factors may lead to the opposite behavior [8-10].

The lone branched side chain along the 2 nm backbone subunit-repeat distance is unusual as most

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polymers with such long repeat lengths have multiple alkyl chains with more alkyl chain material per polymer repeat unit. PCA has been reported to have a high solubility, nearly perfect internal quantum efficiency [11], high-power conversion efficiency (>7.2%) [12,13] in samples annealed below 80 °C and excellent thermal stability [14], with operating lifetimes estimated to be 7 years [15]. For thin films, no crystalline peaks were detected in the X-ray scattering profiles in studies (conventional source), for samples annealed as high as 400 °C [14]. The electrochemical polymerization of heterocyclic monomers to yield electronically conducting and redox electroactive polymers is well documented. Electrically conducting polymers have been considered for numerous applications including charge dissipation coatings [15], organic thin-film transistors [16], and conducting textiles [17]. The use of electrically conducting polymers in electrochromic devices, as materials that possess the ability to reversibly change color by altering redox state, has emerged [18-23]. Many conjugated polymers are colored in the neutral state since the energy difference between the σ -bonding orbitals (conduction band) and the σ^* antibonding orbitals (valence band) lies within the visible region [24-28]. Upon oxidation, the intensity of the σ -to- σ^* transition decreases, and two low-energy transitions emerge to produce a second color. For example poly(3-methylthiophene) is red in the neutral state and blue in the oxidized state [29-35]. While most electroactive

polymers have the ability to exhibit two colors, only a select few show multiple color states. Due to its accessibility and ease of handling, polyaniline (PANI) has become the conducting polymer of choice for many technological applications and has been studied extensively for its potential use as an electrochromic material [36-44]. PANI is able to exist in three distinct reversible colored states; specifically yellow in the neutral state, green at 0.5 V vs SCE, and dark blue at 0.8V [45-49]. With multiple cycles, PANI tends to lose its ability to access these multicolor states. It has been shown, after 300 cycles between -0.2 and 1.0 V vsSCE, which the electrochromic activity of the film decreases as the color converts to semitransparent black with little change incolor with variance in potential [50-56]. An alternative to PANI for a multiply colored electrochromicpolymer is polycarbazole. Previous work hasshown poly(*N*-substituted carbazoles) to be clear colorless when neutral, green at an applied potential of 0.7. V vs SCE, and blue at 1.0 V [57-64]. carbazoles) to be clear colorless when neutral, green at The objective of the present research is to study the electrical and structural properties of all mono-, and di-fluorocarbazolesand their radical cations. All of the possibleofmono-, and di-fluorocarbazoles studied in this work are presented in Figure 1.

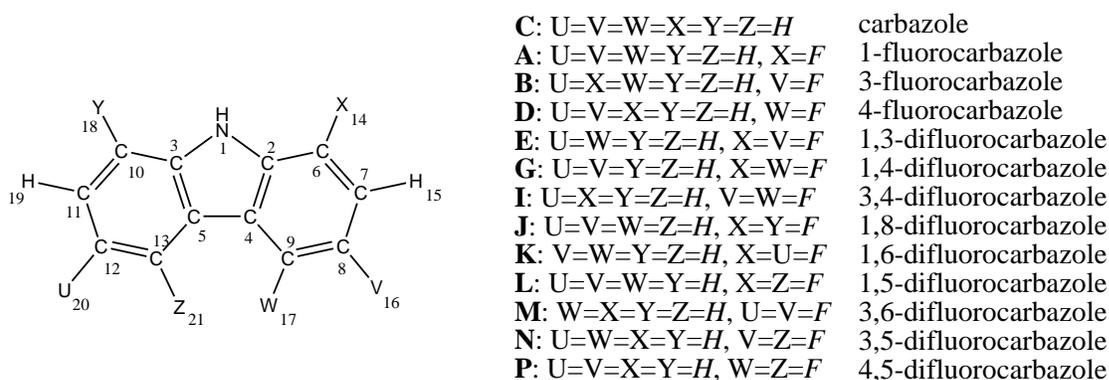


Figure 1: All possible mono-, and di-fluorocarbazoles studied in this work.

Result and discussion

Structural Analysis:

In this section, the electrical and structural properties of mono-, and di-fluorocarbazoles and their related radical cations have been studied. Because of the stabilizing effects of the delocalization of non-bonding p electrons of sulfur atom, it is expected that the carbazole molecules possess a plane structure.

In agreement with this expectation, results of the present calculations show that all mono-, and di-fluorocarbazoles possess planar structures (the optimized values of all dihedral angles of all structures are either 0° or 180°). The optimized structural parameters for neutral and radical cation species, respectively, obtained at the B3LYP/6-311+G and the UB3LYP/6-311+G level of theories for all mono-, and di-fluorocarbazoles are listed in Table 1.

To predict the bonding-characteristic behavior of fluorocarbazole rings in their corresponding polymer chains and to determine the extent of the π -conjugation character of these polymers, we have used the F_n coefficient defined in Equation 1 for each carbazole ring [25]:

$$F_n = 2R_{45}/(R_{24}+R_{35})(1)$$

where R_{45} is the length of C_4-C_5 bond (formally single bond) and $[(R_{24}+R_{35})/2]$ is the average length of C_2-C_4 and C_3-C_5 bonds (formally double bonds) in the carbazole ring. The calculated values of the F_n coefficient for carbazole, all mono-, and di-fluorocarbazoles and their radical cations are listed in Table 1. As shown in this table, F_n coefficient has the following trend for all molecules:

$$J > N > \text{Carbazole} > B > P > L > I = D > M = E > A > G > K$$

And for all molecular radical cations, values of the F_n coefficient has the following trend:

$$D > M > L > J > A > G > \text{Carbazole} > I > P > N > E > K = B$$

As this table shows, 1,6-difluorocarbazole has the smallest value of the F_n coefficient. Therefore, it can be suggested that the double bonds in 1,6-difluorocarbazole are more delocalized.

Electropolymerization process for each molecular radical cation is obtained from C_7 and C_{11} linkages, so it can be said that in a compound the greater spin density in C_7 and C_{11} positions is, the higher electropolymerization rate will be.

Table 1. B3LYP/6-311+G optimized values of bond lengths (Å) and the F_n coefficient for carbazole and mono-, and di-fluorocarbazoles.

Molecule	C_4-C_5	C_2-C_4	C_3-C_5	F_n
Carbazole	1.455	1.453	1.355	1.037
	1.413	1.387	1.432	1.002
A	1.353	1.445	1.353	0.967
	1.415	1.386	1.411	1.012
B	1.362	1.221	1.435	1.023
	1.434	1.570	1.497	0.935
D	1.359	1.423	1.362	0.976
	1.469	1.383	1.392	1.059
E	1.356	1.426	1.357	0.974
	1.359	1.497	1.362	0.951
G	1.351	1.438	1.362	0.965
	1.410	1.379	1.410	1.011
I	1.358	1.424	1.358	0.976
	1.413	1.387	1.454	0.995
J	1.333	1.435	1.353	1.434

	<i>1.414</i>	<i>1.356</i>	<i>1.411</i>	<i>1.022</i>
K	1.454	1.431	1.352	0.958
	<i>1.430</i>	<i>1.383</i>	<i>1.390</i>	<i>0.935</i>
L	1.367	1.435	1.353	0.981
	<i>1.433</i>	<i>1.388</i>	<i>1.413</i>	<i>1.023</i>
M	1.366	1.428	1.376	0.974
	<i>1.432</i>	<i>1.376</i>	<i>1.421</i>	<i>1.024</i>
N	1.487	1.431	1.363	1.064
	<i>1.367</i>	<i>1.386</i>	<i>1.431</i>	<i>0.970</i>
P	1.398	1.427	1.365	1.001
	<i>1.375</i>	<i>1.376</i>	<i>1.448</i>	<i>0.974</i>

Corresponding values for the related radical cations optimized with UB3LYP/6-311+G are given in the lower row with italic fonts. See Figure.1 for definitions of bond lengths.

The spin-density distribution over the ring atoms of fluorocarbazole radical cations have been calculated and presented in Table 2. As shown in this table, it is obvious that K monomer has the maximal spin density on position C₇. This means that the electropolymerization of 1,6-difluorocarbazole (K) can be more favorable ratio with respect to other molecules.

Charge- and Spin-Distribution Analysis:

Natural Bond Orbital (NBO) charges in this series of fluorocarbazoles and their cations have been calculated and reported in Table 2. In addition, the spin-density distribution over the ring atoms of the fluorocarbazole cation radicals have been calculated and presented in Table 3. For all mono-, and di-fluorocarbazoles and their radical cations, the positive charge is distributed mainly on the C₇ and C₁₁ positions in Figure 1, whereas spin density is distributed mainly on the C₆ and C₁₀ positions in Figure 1. In both series of molecules and their radical cations, charge- and spin-density distributions have similar trends with the number and position of the substituted fluorine atoms. The distribution charge on the C₇ atom in K monomer radical cation shows that possibly, the electropolymerization rate of K monomer is greater than carbazole and other fluorocarbazoles. Consequently, it can be said that compared with other

fluorocarbazoles the electric conductivity of polymer blends obtained from the K monomer is higher than other molecules.

At this point, it seems useful to remember some useful aspects concerning the NBO analysis, which was effectively used in this work. In the NBO analysis, the electronic wavefunctions are interpreted in terms of a set of occupied Lewis and a set of unoccupied non-Lewis localized orbitals. The delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydberg) non-Lewis NBO orbitals corresponds to a stabilizing donor-acceptor interaction, which is taken into consideration by examining all possible interactions between filled (donor) and empty (acceptor) orbitals and then evaluating their energies by second order perturbation theory. Accordingly, the delocalization effects (or donor-acceptor charge transfers) can be estimated from the presence of off-diagonal elements of the Fock matrix in the NBO basis. NBOs closely correspond to the picture of localized bonds and lone pairs as basic units of the molecular structure so that is possible to conveniently interpret ab initio wavefunctions in terms of the classical Lewis structure concepts by transforming these functions to NBO form.

Table2: Natural Bond Orbital charge distribution on nitrogen and carbon atoms in the B3LYP/6-311+Goptimized structures of carbazole and mono-, and di-fluorocarbazoles(and their radical cations).

Molecule	$-\delta_N$	δ_{C2}	δ_{C3}	δ_{C4}	δ_{C5}	δ_{C7}	δ_{C11}
Carbazole	0.801 (0.262)	0.169 (-0.014)	-0.263 (0.034)	0.182- (-0.182)	-0.257 (0.005)	0.282 (0.254)	-0.263 (0.134)
A	0.797 (0.572)	0.113 (0.189)	0.360 (0.467)	-0.251 (-0.257)	-0.238 (-0.040)	0.296 (-0.264)	-0.250 (-0.279)
B	0.797 (0.573)	0.187 (0.246)	-0.329 (-0.264)	0.436 (0.450)	-0.321 (-0.091)	0.264 (-0.180)	-0.277 (-0.142)
D	0.806 (0.582)	0.156 (0.227)	-0.242 (-0.158)	-0.246 (-0.221)	0.369 (0.533)	0.346 (0.331)	-0.242 (-0.158)
E	0.795 (0.565)	0.127 (0.196)	0.301 (0.387)	0.373 (0.368)	-0.306 (0.095)	0.379 (-0.067)	-0.273 (0.334)
G	0.801 (0.581)	0.099 (0.180)	0.380 (0.465)	-0.313 (-0.302)	0.386 (0.537)	0.361 (0.315)	-0.250 (-0.279)
I	0.790 (0.322)	0.131 (0.375)	0.347 (-0.327)	-0.233 (0.186)	-0.303 (0.145)	0.422 (-0.260)	-0.316 (0.177)
J	0.794 (0.565)	0.057 (0.141)	0.373 (0.455)	-0.265 (-0.255)	-0.220 (-0.031)	0.465 (0.355)	0.374 (0.455)
K	0.798 (0.585)	0.171 (0.239)	-0.314 (-0.259)	0.376 (0.410)	0.310 (0.488)	0.632 (0.329)	0.257 (0.245)
L	0.790 (0.565)	0.202 (0.256)	-0.344 (-0.245)	0.451 (0.443)	-0.382 (-0.140)	0.551 (0.443)	-0.344 (-0.245)
M	0.798 (0.576)	0.113 (0.184)	0.316 (0.381)	0.316 (0.330)	0.325 (0.488)	0.348 (0.320)	-0.247 (-0.162)
N	0.794 (0.574)	0.110 (0.207)	0.315 (0.418)	0.360 (0.365)	-0.315 (-0.159)	0.368 (0.468)	-0.316 (-0.384)
P	0.791 (0.569)	0.072 (0.147)	0.314 (0.366)	0.361 (0.380)	-0.288 (-0.089)	0.448 (0.357)	0.364 (0.472)

Corresponding values for the related radical cations optimized with UB3LYP/6-311+G are given in the lower row. See Figure.1 for definitions of atoms.

Table3: Distribution of spin density over nitrogen and carbon atoms in UB3LYP/6-311+Goptimized structures of carbazole and mono-, and di-fluorocarbazolesradical cations.

Molecule	N_1	C_2	C_3	C_4	C_5	C_7	C_{11}
Carbazole	-0.105	0.554	0.547	0.193	0.046	0.146	0.448
A	-0.099	0.432	0.432	0.193	0.193	0.223	0.415
B	0.030	0.554	0.395	0.395	0.293	0.229	0.328
D	-0.094	0.429	0.423	0.423	0.193	0.332	0.489

E	-0.088	0.426	0.426	0.396	-0.090	0.175	0.481
G	-0.099	0.416	0.416	0.416	0.078	0.078	0.446
I	-0.105	0.554	0.554	0.554	0.004	0.031	0.428
J	-0.083	0.429	0.429	0.429	0.026	0.008	0.429
K	-0.074	0.432	0.432	0.193	0.148	0.011	0.582
L	-0.088	0.426	0.426	-0.090	0.034	0.123	0.446
M	-0.094	0.193	0.193	0.193	0.078	-0.090	0.434
N	-0.007	-0.090	-0.090	-0.090	0.001	0.443	0.421
P	-0.099	0.078	0.078	0.078	0.008	0.316	0.399

For each donor NBO (i) and acceptor NBO (j), the stabilization energy (E_2) associated with $i \rightarrow j$ delocalization is explicitly estimated by the equation:

$$E_2 = \Delta E_{ij} = q_i \frac{F_{(i,j)}^2}{\epsilon_j - \epsilon_i} \quad (2)$$

Where q_i is the i th donor orbital occupancy, ϵ_i and ϵ_j are diagonal elements (orbital energies), and $F_{(i,j)}$ are

off-diagonal elements, respectively, associated with the NBO Fock matrix.

Electric Dipole Moments:

Orientations of the polymer chains in the condensed phase are the most important parameters affecting the electric charge transport properties of polymers so that the electrical conductivity of a polymer chain is altered when its orientation and consequently its symmetry and non-isotropic interactions are changed.

Table4: Electric dipole moments, polarizability tensor elements and ionization potentials calculated at B3LYP/6-311+G level of theory for the optimized structures of carbazole and mono-, and di-fluorocarbazoles.

Molecule	Electric dipole moment (D)			Polarizabilities (Å)					IP (eV)
	μ_x	μ_y	μ_{tot}	α_{xx}	α_{yy}	α_{zz}	α_{xy}	α_{ave}	
Carbazole	0.00	-1.45	2.16	73.65	69.14	38.83	-0.33	60.18	15.75
A	0.98	-0.65	0.25	73.79	70.28	38.86	0.93	60.33	15.67
B	0.50	-1.341	1.43	73.65	73.85	41.01	2.96	60.24	15.87
D	-1.45	-2.16	2.30	71.96	69.14	37.98	-1.85	60.32	15.82
E	-0.65	-0.25	0.70	68.46	68.55	38.83	-2.60	60.49	15.84
G	-1.45	-2.16	2.40	69.05	73.07	38.83	-0.02	60.56	15.64
I	-1.75	-1.50	2.50	71.52	70.28	38.86	4.20	60.72	17.21
J	0.31	-2.39	3.70	72.20	73.85	41.01	3.11	61.49	18.10
K	-2.39	-0.99	2.65	73.65	69.14	37.98	-0.33	60.26	15.79
L	-0.99	2.30	1.20	71.96	72.81	37.47	-2.66	62.75	17.03
M	-0.65	-0.25	1.70	69.05	68.55	38.83	-1.60	62.49	18.81
N	-1.45	-2.16	2.60	71.52	73.07	38.83	3.11	62.76	18.61
P	-1.75	-4.50	2.70	78.20	70.28	38.86	-0.33	63.22	19.21

$\mu_z, \alpha_{xz},$ and α_{yz} are essentially zero for all compounds because of the planar structure. The values of α_{ave} have been calculated using the $\alpha_{ave} = (1/3)(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ relation.

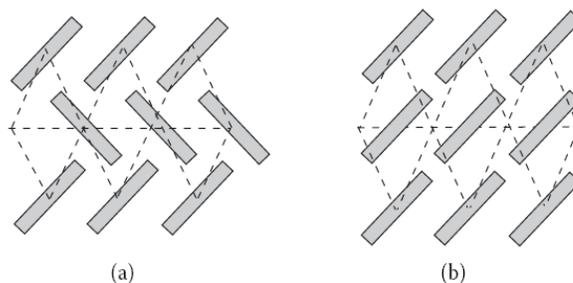


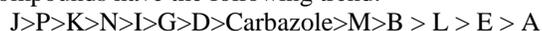
Figure 2: Illustration of stacking arrangements proposed for polycarbazole. Oriented chains extend into and out of the page: (a) herringbone stacking arrangement, (b) lamellar stacking arrangement.

Chemically synthesized polycarbazoles powders exhibit a partially crystalline structure in which the chains align and pack in a herringbone arrangement (Figure 2) in the crystalline regions. These overall interactions can be well expressed in terms of interactions between local dipole moments of monomers. The local alignment of monomers' dipole moments in solution with respect to the orientation of the polymer chain determines the electrochemical properties of the polymer formed on an electrode surface.

In addition, the orientation of monomers in the double layer of the solution in an electropolymerization cell depends on both size and direction of the dipole moment vectors of both monomers and polymer chains.

It is necessary to study the dipole moments of these mono- and di-fluorocarbazoles to be able to predict their electropolymerization properties. The size of the dipole moment vector and its components calculated for mono-, and di-fluorocarbazoles in this study are presented in Table 4.

An analysis of calculated dipole moments shows that the orientation of the dipole moment vector is toward nitrogen atom for all mono-, and di-fluorocarbazoles. The size and direction of the dipole moment vector is more dependent on the position (symmetry) of substituent than its number. It can also be seen in Table 4 that the dipole moments for all compounds have the following trend:



The size of the dipole moment vector for monomers J and P is greater than other compounds. Therefore, compounds J and P have a high solubility in polar solvents. These characteristics increase the efficiency of electrochemical polymerization processes of these monomers. Moreover, it can be seen in Table 3 that carbazole has a low solubility in polar solvents.

Ionization Potentials:

The first step in the electropolymerization of conductive polymers is formation of intermediate radical cations from monomers which can be considered as an ionization reaction:



Where M and $M^{\bullet+}$ denote monomer and its radical cation respectively. So, stability of intermediate radical cations has an important role in the electropolymerization process. Therefore, it is useful to calculate electronic energy difference between the neutral monomer (as the initial species) and positively charged monomer (as the intermediate). This energy difference is proportional to Ionization Potential (IP) of the monomer. Calculated values of IP for mono-, and di-fluorocarbazoles based on Equation 2 are presented in Table 4. The trend of electrochemical stability of these monomers is:



Since ionization potential energies are directly proportional to the electrochemical oxidation potentials of the compounds, it can be said that the electrochemical stability of monomer P is greater than other compounds and the 1,6-difluorocarbazole has a low electrochemical stability.

Electric Polarizabilities:

Values of polarizabilities of compounds containing halogen are used to interpret light scattering and intensities of vibrational Raman spectra. Values of exact electrical polarizabilities and average of polarizabilities (α_{ave}) for carbazole and all mono-, and di-fluorocarbazoles have been calculated and listed in Table 4. Based on this table, it can be claimed that with an increase in the number of fluorine atoms on the carbazole ring, polarization values will increase as well. The zero values obtained for polarizabilities α_{xz} and α_{yz} are consequences of the planar structure. The small values of α_{xy} polarizabilities indicate that the delocalization strength of the π -system of the ring dominates the anisotropic effects on asymmetric mono-, and di-fluorocarbazoles.

Zero-Point and Electronic Energy:

Zero-Point vibrational Energy (ZPE) and total electronic (E_{el}) energies ($E_0 = ZPE + E_{el}$) for carbazole and all mono-,

and di-fluorocarbazoles calculated on the B3LYP/6-311+G//B3LYP/6-311+G level of theory. For single-point energy calculations, both HF/6-311+G// B3LYP /6-311+G and MP2/6-311+G// B3LYP /6-311+G method were used and are given in Table 4. Studies on the B3LYP/6-311+G, HF/6-311+G// B3LYP /6-311+G, and MP2/6-311+G// B3LYP /6-311+G of theory show that the ZPE for

carbazole is greater than other compounds, as a result the relative thermal stability of carbazole is higher than other compounds. Also the Ground-State electronic energies for all mono-, and di-fluorocarbazoles calculated on the B3LYP/6-311+G, MP2/6-311+G and HF/6-311+G levels of theory listed in Table 5.

Table 5: (a) Electronic Energies and Zero Point Energy (in Hartree/particle), (b) Ground-State Electronic Energies of formation, calculated for representative mono-, and di-fluorocarbazoles using HF, MP2, and DFT-B3LYP Levels of theory with the 6-311+G basis Set a) Electronic energies and zero point energy

Molecule	B3LYP/6-311+G		HF/6-311+G	MP2/6-311+G
	E_{ele}	ZPE	E_{ele}	E_{ele}
Carbazole	-180523.1999	72.53408	-179340.9237	-179974.4320
A	-242814.3379	67.55418	-241387.8333	-242145.9394
B	-242815.0244	67.42703	-241389.4548	-242146.3778
D	-242813.1168	67.35701	-241386.5930	-242144.6282
E	-305101.3853	62.53973	-303431.6326	-304313.2790
G	-305103.4741	62.33581	-303432.8738	-304315.4874
I	-305104.9276	62.39066	-303434.9649	-304316.5978
J	-305104.5679	62.51639	-303433.9852	-304316.7612
K	-305100.3653	62.31755	-303430.5316	-304086.2605
L	-305105.9751	62.28170	-303437.2701	-304317.4974
M	-367386.1505	57.42337	-365472.1923	-366478.6120
N	-367391.2186	57.33561	-305478.1417	-366483.3254
P	-367390.5882	57.47872	-365476.4989	-366482.9836

b) Ground-State Electronic Energies			
Molecule	B3LYP/6-311+G	HF/6-311+G	MP2/6-311+G
	ΔE_{ele} (kcal/mol)	ΔE_{ele} (kcal/mol)	ΔE_{ele} (kcal/mol)
Carbazole	-805.19	793.92	-799.43
A	-428.33	413.83	-421.93
B	-428.02	-413.45	-421.37
D	-428.11	413.59	-421.62
E	-510.38	-343.63	-431.27
G	510.47	343.87	-431.48
I	510.92	343.96	431.59
J	-514.56	343.98	-431.76
K	510.36	343.53	408.26
L	-515.97	343.27	-431.49

M	-738.15	-547.19	-647.61
N	-739.21	547.14	-648.32
P	-739.58	547.49	-648.98

Structural analysis of radical cations of the oligo(1,6-difluorocarbazole):

Results of the calculations reported in a previous work show that an infinite neutral chain of a carbazole ring in a 3-D periodic arrangement is planar. This can be explained in terms of attractive interactions between properly oriented electric dipole moments of adjacent rings. Therefore, it can be assumed that radical cation of the K-dimer is planar. On the basis of this fact, we have optimized structures of both the singly ionized C-dimer and K-dimer upon setting a planar initial structure. The optimized structures of the C-

dimer (where R=H) and K-dimer (where R=F) are shown in Figure 3.

An analysis of the values of the F_n coefficient of the C tetramer and K tetramer, reported in Table 6, shows that radical cation of K tetramer chain has smaller F_n coefficient character than the C tetramer. The radical cation of the K tetramer shows a ring current localized in the central part of the chain, whereas the aromatic conjugation in this oligomer is concentrated mainly on the terminal rings. This result is confirmed by inspecting the values of the F_n coefficient and the inter-ring bond lengths reported in Table 6.

Table 6: Values of the bond lengths and F_n coefficient for the B3LYP/3-21G optimized radical cation structure of (a) C-oligomer (mono-, di-, tri-, and tetra-carbazole) and (b) K-oligomer (mono-, di-, tri-, and tetra-(1,6-difluorocarbazole) See Figure 1 for definitions of atoms.

a) Radical cation structure of C-oligomer

n	C ₄ -C ₅	C ₂ -C ₄	C ₃ -C ₅	F_n
1	1.510	1.330	1.330	1.135
2	1.501	1.335	1.337	1.123
3	1.495	1.339	1.340	1.116
4	1.497	1.343	1.342	1.115

b) Radical cation structure of K-oligomer

n	C ₄ -C ₅	C ₂ -C ₄	C ₃ -C ₅	F_n
1	1.409	1.421	1.421	0.991
2	1.398	1.424	1.425	0.981
3	1.387	1.429	1.428	0.971
4	1.376	1.431	1.432	0.961

n is the progressive number of the carbazole molecule in the chain

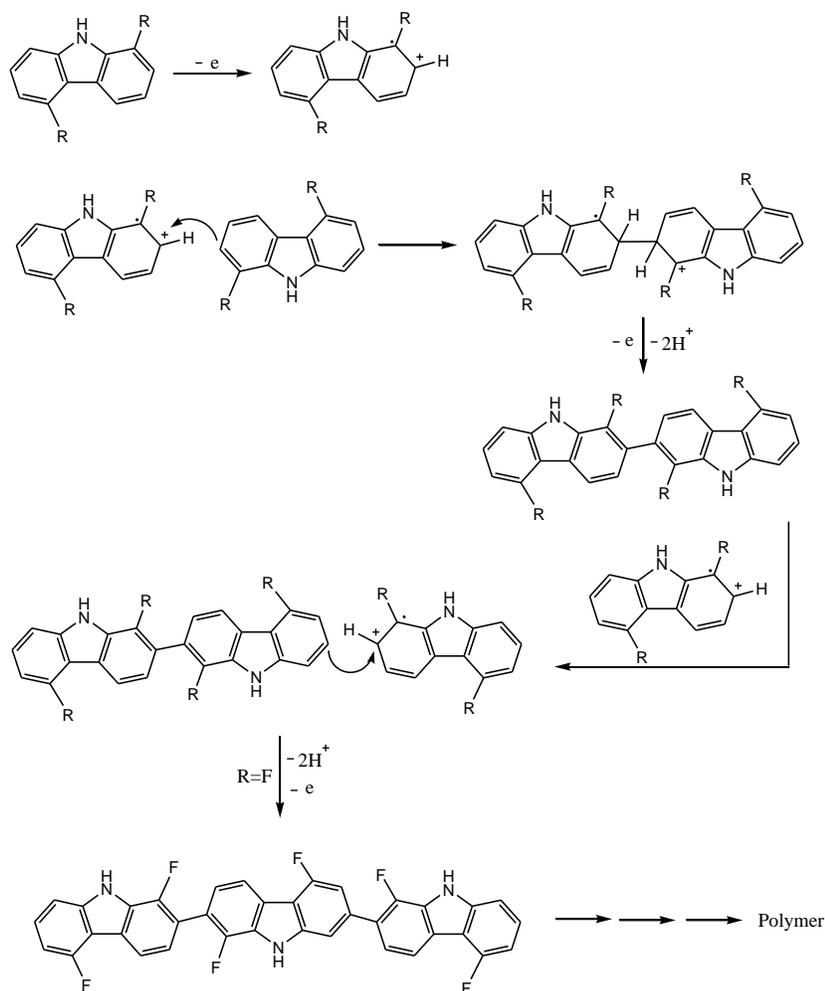


Figure 3: Polymerization of carbazole (where R = H or a substituent)

Computational Procedures:

Ab initio calculations were carried out using B3LYP/6-311+G, HF/6-311+G// B3LYP /6-311+G, and MP2/6-311+G// B3LYP /6-311+G levels of theory with the GAUSSIAN 98 package of programs [65,66] implemented on a Pentium-PC computer with a 7300 MHz processor. Initially, structures of representative mono-, di-fluorocarbazoles were fully optimized using gradient procedures at restricted Hartree-Fock, perturbation theory MP2, and hybrid density functional B3LYP levels of theory using the 6-311+G basis set. The natures of the optimized stationary points were all characterized by frequency calculations at the same level of theory with the same basis set. The analysis of the results showed that all methods characterized all of the optimized structures obtained in this study as minima on the potential energy surface without any negative mode. A preliminary basis set test carried out

at the HF level of theory showed that 6-311+G is the best basis set that can be used within our available hardware/software facilities in a reasonable time. Structures of representative mono-, and di-fluorocarbazoles were optimized using B3LYP/6-311+G method. The vibrational analysis showed that all structures correspond to local minima in potential energy surface. Atomic charges were calculated using Natural Bond Orbital (NBO) method [67,68].

Conclusion

B3LYP method with 6-311+G basis set calculations have been carried out successfully to study the structural, electric and spectroscopic properties of all mono-, and di-fluorocarbazoles. Values of dipole moment, spin density distribution and ionization potential have been calculated and analyzed. The analysis of these data showed that the 1,6-difluorocarbazole (K molecule) has the smallest value

of the F_n coefficient, it can be suggested that double bonds in this molecule are more delocalized. The electrochemical stability of carbazole and 1-fluorocarbazole are greater than other compounds, zero-point energy for carbazole is greater than other molecules, and thermal stability of carbazole is higher than other compounds. The electrochemical stability of 4,5-difluorocarbazole is greater than other compounds and the 1,6-difluorocarbazole has a low electrochemical stability. Also, 1,8-difluorocarbazole and 4,5-difluorocarbazole have a high solubility in polar solvents. Accordingly, K monomer (1,6-difluorocarbazole) is the best candidate monomer among all mono-, and di-fluorocarbazoles for the synthesis of corresponding conductive polymers with modified characteristics. The synthesis feasibility, experimental measurement and thermo chemical stability of these mono-, and di-fluorocarbazoles are interesting subjects for study.

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References

- [1] Sirringhaus, H. *et al. Nature.*, **1999**, 401, 685–688.
- [2] McCulloch, I. *et al. Nature Mater.*, **2006**, 5, 328–333.
- [3] Yan, H. *et al. Nature*, **2009**, 457, 679–686.
- [4] Winokur, M. J.; Chunwachirasiri, W. *J. Polym. Sci B Polym. Phys.*, **2003**, 41, 2630–2648.
- [5] Heeger, A. J. *Chem. Soc. Rev.*, **2010**, 39, 2354–2371.
- [6] Coffin, R. C.; Peet, J.; Rogers, J.; Bazan, G. C. *Nat. Chem.*, **2009**, 1, 657–661.
- [7] Szarko, J. M. *et al. Adv. Mater.*, **2010**, 22, 5468–5472.
- [8] Yang, L.; Zhou, H.; You, W. *J. Phys. Chem. C.*, **2010**, 114, 16793–16800.
- [9] Shi, Q. *et al. Macromolecules.*, **2011**, 44, 4230–4240.
- [10] Gadisa, A. *et al. Adv. Funct. Mater.*, **2009**, 19, 3300–3306.
- [11] Blouin, N.; Michaud, A.; Leclerc, M. *Adv. Mater.*, **2007**, 19, 2295–2300.
- [12] Park, S. H. *et al. Nat. Photon.*, **2009**, 3, 297–302.
- [13] Sun, Y. *et al. Adv. Mater.*, **2011**, 23, 2226–2230.
- [14] Cho, S. *et al. Adv. Mater.*, **2010**, 22, 1253–1257.
- [15] Heywang, G.; Jonas, F. *Adv. Mater.*, **1992**, 4, 116
- [16] Dodabalapur, A.; Torsi, L.; Katz, H. E. *Science*, **1995**, 268, 270.
- [17] Kuhn, H. H.; Child, A. D.; Kimbrell, W. C. *Synth. Met.*, **1995**, 71, 2139.
- [18] Druy, M. A.; Seymour, R. J. *J. Phys.*, **1983**, 595.
- [19] Haynes, D. M.; Hepburn, A. R.; Goldie, D. M.; Marshall, J. M.; Pelter, A. *Synth. Met.*, **1993**, 55, 839.
- [20] Panero, S.; Passerini, S.; Scrosati, B. *Mol. Cryst. Liq. Cryst.*, **1993**, 229, 97.
- [21] Gustafsson, J. C.; Inganäs, O.; Andersson, A. M. *Synth. Met.*, **1994**, 62, 17.
- [22] Hyodo, K. *Electrochim. Acta.*, **1994**, 39, 265.
- [23] Nawa, K.; Imae, I.; Noma, N.; Shirota, Y. *Macromolecules.*, **1995**, 28, 723.
- [24] Kobayashi, T.; Yoneyama, H.; Tamura, H. *J. Electroanal. Chem.*, **1984**, 177, 293.
- [25] Shirani Il Beigi, H.; *Can. J. Chem.*, **2012**, 90, 902–914.
- [26] Glarum, S.H.; Marshall, J. H. *J. Electrochem. Soc.*, **1987**, 134, 2160.
- [27] Stilwell, D. E.; Park, S.M. *J. Electrochem. Soc.*, **1988**, 135, 2497.
- [28] Stilwell, D. E.; Park, S.M. *J. Electrochem. Soc.*, **1989**, 136, 427.
- [29] Chinn, D.; DuBow, J.; Liess, M. *Chem. Mater.*, **1995**, 7, 1504.
- [30] Faid, K.; Ades, D.; Siove, A.; Chevrot, C. *J. Chim. Phys.*, **1992**, 89, 1019.
- [31] Shirani Il Beigi, H.; Ghanbarpour, P. *J. Str. Chem.*, **2014**, 55, 217–222.
- [32] Faid, K.; Ades, D.; Siove, A.; Chevrot, C. *Synth. Met.*, **1994**, 63, 1578.
- [33] Ambrose, J.G.; Nelson, R. F. *J. Electrochem. Soc.*, **1968**, 115, 1159.
- [34] Desbene-Monvernay, A.; Lacaze, P.C.; Dubois, J.E. *J. Electroanal. Chem.*, **1981**, 129, 229.
- [35] Cattarin, S.; Mengoli, G.; Musiani, M. M.; Schreck, B. *J. Electroanal. Chem.*, **1988**, 246, 87.
- [36] Mengoli, G.; Musiani, M. M.; Schreck, B.; Zecchin, S. *J. Electroanal. Chem.*, **1988**, 246, 73.
- [37] Qiu, Y.J.; Reynolds, J. R. *J. Electrochem. Soc.*, **1990**, 137, 900.
- [38] Grazulevicius, J. V.; Kublickas, R. *Eur. Polym. J.*, **1991**, 27, 1411.
- [39] Hepburn, A. R.; Marshall, J. M.; Maud, J. M. *Synth. Met.*, **1991**, 41, 2935.
- [40] Geibler, U.; Hallensleben, M. L. *Synth. Met.*, **1993**, 55, 1662.
- [41] Mazeika, R.; Grazulevicius, J. V.; Kavaliunas, R.; Kreiveniene, N. *Eur. Polym. J.*, **1994**, 30, 319.
- [42] Danieli, R.; Ostojica, R.; Tiecco, M.; Zamboni, R.; Taliani, C. *J. Chem. Soc., Chem Commun.*, **1986**, 1473.

- [43] Ferraris, J. P.; Skiles, G. D. *Polymer.*, **1987**, *28*, 179.
- [44] Tanaka, S.; Kaeriyama, K.; Hiraide, T. *Makromol. Chem., Rapid Commun.*, **1988**, *9*, 743.
- [45] Kaeriyama, K.; Tanaka, S. *Makromol. Chem.*, **1988**, *189*, 1755.
- [46] Ferraris, J. P.; Andrus, R. G.; Hrcir, D. C. *J. Chem. Soc., Chem. Commun.*, **1989**, 1318.
- [47] Pelter, A.; Maud, J. M.; Jenkins, I.; Sadeka, C.; Coles, G. *Tetrahedron Lett.*, **1989**, *30*, 3461.
- [48] Roncali, J.; Gorgues, A.; Jubault, M. *Chem. Mater.*, **1993**, *5*, 1456.
- [49] Haynes, P. M.; Hepburn, A. R.; Goldie, D. M.; Marshall, J. M.; Pelter, A. *Synth. Met.*, **1993**, *55*, 839.
- [50] Lorcy, D.; Cava, M. P. *Adv. Mater.*, **1992**, *4*, 562.
- [51] Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Chem. Soc., Chem. Commun.*, **1994**, 1585.
- [52] Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. *Chem. Mater.*, **1996**, *8*, 882-889.
- [53] Child, A. D.; Sankaran, B.; Larmat, F.; Reynolds, J. R. *Macromolecules.*, **1995**, *28*, 6571.
- [54] Reynolds, J. R.; Katritzky, A. R.; Soloduchko, J.; Belyakov, S.; Sotzing, G.; Pyo, M. *Macromolecules.*, **1994**, *27*, 7225.
- [55] Reynolds, J. R.; Child, A. D.; Ruiz, J. P.; Hong, S. Y.; Marynick, D. S. *Macromolecules.*, **1993**, *26*, 2095.
- [56] Ruiz, J. P.; Dharia, J. R.; Reynolds, J. R.; Buckley, L. J. *Macromolecules.*, **1992**, *25*, 849.
- [57] Reynolds, J. R.; Ruiz, J. P.; Child, A. D.; Nayak, K.; Marynick, D. S. *Macromolecules.*, **1991**, *24*, 678.
- [58] Alexander, C.; Andersson, H. S.; Andersson, L. I.; Ansell, R. J.; Kirsch, N.; Nicholls, I. A.; O'Mahony, J.; Whitcombe, M. J. *J. Mol. Recognit.*, **2006**, *19*, 106-180.
- [59] Algar, W. R.; Massey, M.; Krull, U. J. *Trends Anal. Chem.*, **2009**, *28*, 292-306.
- [60] Allan, I. J.; Vrana, B.; Greenwood, R.; Mills, D. W.; Roig, B.; Gonzalez, C. *Talanta.*, **2006**, *69*, 302-322.
- [61] Ambrosi, A.; Merkori, A.; de la Escosura-Muniz, A. *Trends Anal. Chem.*, **2008**, *27*, 568-584.
- [62] Arora, K.; Sumana, G.; Saxena, V.; Gupta, R. K.; Gupta, S. K.; Yakhmi, J. V.; Pandey, M. K.; Chand, S.; Malhotra, B. D. *Acta.*, **2007**, *594*, 17-23.
- [63] Winokur, M. J. In *Handbook of Conducting Polymers. Conjugated Polymers. Theory, Synthesis, Properties and Characterisation*, 3rd edition, T. A. Skotheim and Reynolds, J. R. (Eds), CRC Press, Boca Raton, **2007**, 17-27.
- [64] Waltman, R. J.; Diaz, A. F.; Bargon, J. *J. Phys. Chem.*, **1984**, *88*, 4343-4357.
- [65] Gross, E. K.; Dreiz, R. M. *Density Functional Theory*; Plenum Press, New York, **1995**.
- [66] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. GAUSSIAN 98 (Revision A3), Gaussian Inc, Pittsburgh, PA, **1998**.
- [67] F. Weinhold, "Natural Bond Orbital Methods," in *Encyclopedia of Computational Chemistry*, P. v.R. Schleyer, N. L. Allinger, T. Clark, J. Gasteiger, P. A. Kollman, H. F. Schaefer III, P. R. Schreiner (Eds.), (John Wiley & Sons, Chichester, UK, **1998**, *3*, 1792-1811.
- [68] F. Weinhold (ed.), *NBO 5.0 Program Manual*, Theoretical Chemistry Institute, Univ. Wisconsin-Madison, **2001**.