Effect of aniline substitutions on polyaniline HOMO/LUMO band gap

M. S. Rahmanifar

Faculty of Basic Sciences, Shahed University, P. O. Box 19575-361, Tehran, Iran

Key words: Conducting polymer, Polyaniline, Band Gap

Introduction:

Polyaniline (PANI) is a typical organic semiconductor which has attracted great attention in fundamental science and industry, because its properties can be reversibly controlled by both oxidation/reduction of amine/imine groups and protonation/deprotonation. PANI has three redox forms, leucoemeraldin (LE), emeraldine (E) and pernigraniline (PG) that can be protonated and leading to drastic changes in different properties such as electrical, optical and etc. The rich electronic properties of PANI systems as well as their invironmental stability and low cost make PANI an attractive material for applications in many areas such as rechargeable batteries [1], supercapacitors [2], sensors [3] and etc. The arisen properties are considerably affected by two groups of factors, first structural factors and second chemical factors that rearrange the interamolecular force. Here in, we establish a bridge between structural parameters of a substituted polyaniline with its conducting properties, then compare it with unsubstituted polymer.

Computational Details:

Geometries and band gaps of PANI and SO_3H, $COOH$ and NH_2 substituted PANI oligomers up to octamer have been systematically calculated and analyzed using molecular mechanics and semiempirical methods, respectively, by GAUSSIAN 98 program. On the basis of fully optimized geometries of neutral and charged forms of PANI (substituted/unsubstituted) oligomers, excitation energies are calculated. Band gaps are also approximated by extrapolating the HOMO/LUMO difference and extrapolated to the band gap value of the infinite chain. The doped form of PANI (two positive charges per four aniline units) has been computed with band gap approximation from an extrapolation of the tetramer and octamer.

Results and Discussion:

It is indicated that the phenyl ring torsional angles and the pyramidality (the sum of the bond angles around a nitrogen atom) play an important role in determining structures of organic compounds containing an amine group. From the crystal structure study of diphenylamine (phenyl capping aniline dimer), the measured value of the interring dihedral angles are in the range of 23° -65°.

At the first, Geometries of all LE oligomers were optimized with MM method and the dihedral angles between phenyl rings calculated and compared with diphenylamine dihedral angles. Then HOMO/LUMO band gaps of oligomers were calculated by AM1 method. Fig. 1 represents the electronic levels of LE base oligomers, addition of every new aniline unit causes hybridization of the energy levels yielding more and more levels until a point is reached at which there are bands rather than discrete levels. Interaction between the electrons of neighboring molecules leads to a three-dimensional band structure. Extrapolated band gaps were obtained by plotting excitation energies from PANI oligomers calculations against the inverse number of aniline units and extrapolating to an infinite number of units as shown in Figure 2. The extrapolated band gap value of LE acid form is smaller than those of LE base oligomers, which may suggest that the LE acid form is more conjugated than LE base.
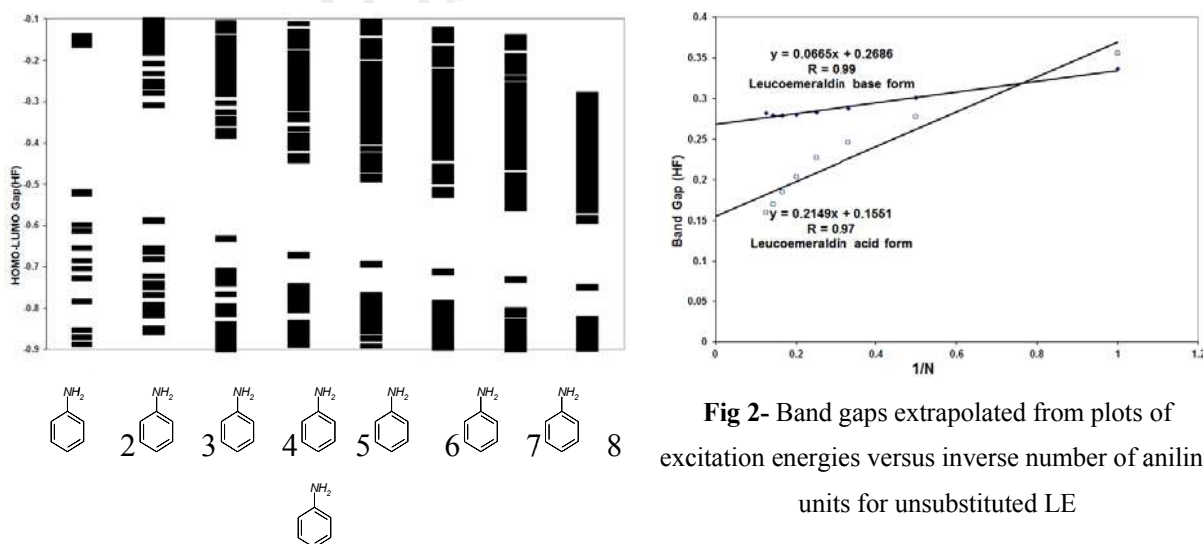

Fig 2- Band gaps extrapolated from plots of excitation energies versus inverse number of aniline units for unsubstituted LE

Fig 1- Calculated energy levels of oligoanilines
with n= 1 to 8 for LE

For PANI other forms, same calculation were carried out and band gaps were extrapolated. Table 1 shows the band gaps of PANI different redox forms in acid and basic stats. This is very close to the experimental observation because insulator to conductor transition occurred for emeraldine protonated form of PANI. For this reason, in the case of substituted PANI only substituted emeraldine (protonated/deprotonated) form were considered. On the other hand, estimation of HOMO/LUMO band gap of substituted PANI only has done for substituted emeraldine and its protonated forms. For comparison of band gaps of substituted emeraldine with unsubstituted, relative values is shown in Table 2.

Table 1- Comparison of extrapolated Band Gaps (HF) Between PANI different redox forms in acid and basic stats

	Base form	Acid form
Leucoemeraldin	0.2686	0.1551
Emeraldine	0.2399	0.0055
Pernigraniline	0.2375	0.0672

Table 2- Comparison of HOMO/LUMO gap of substituted/unsubstituted PANI fractions

	Base form	Acid form
SO_3H	0.60	14
COOH	0.55	4.3
NH_2	0.98	26

Based on the results of table 2 can be concluded that substituted PANI in E acid forms has less conductivity than unsubstituted PANI. This can be related to the phenyl rings torsional angles connected to a nitrogen atom. When the π orbital of the phenyl rings is parallel to each other maximum conductivity is achieved, but substitution on ring cause distortion of the conjugation and band gap is increased.

References:

[1] M. S. Rahmanifar and M. F. Mousavi, M. Shamsipur, M. Ghaemi, "What is the limiting factor in cycle life of Zn-polyaniline rechargeable batteries?"J. Power Sources, 132, 296-301, 2004.

[2]H.R.Ghenaatian, M.F. Mousavi, M.S. Rahmanifar, "High performance battery–supercapacitor hybrid energy storage system based on self-doped polyaniline nanofibers", Synth. Met., 161, 2017-2023, 2011.

[3] M. F. Mousavi, M. Shamsipur, S. Riahi, M. S. Rahmanifar, "Design of a new dodecyl sulfate-selective electrode based on conductive polyaniline", Anal. Sci., 18, 137-140, 2002.