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Exceptional nonlinear optical properties of thiophene and 3,4-ethylenedioxythiophene (EDOT) oligomers – Density Functional Theory (DFT) calculations

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π -conjugated thiophene-based oligomers (Figure) have become the focus of current research in view of their potential applications in molecular electronic devices. The attraction of these organic electronic

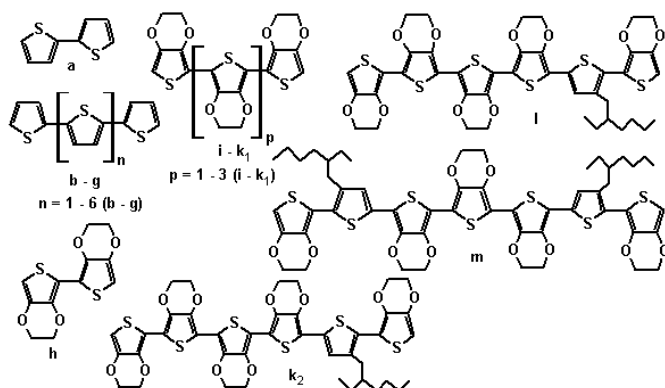


Figure: Thiophene and EDOT oligomers

materials has been their ability to modify chemical structure in ways that could directly impact the properties of the materials when deposited in thin film form. Molecules with large optical non-linearities have become the focus of current research in view of their potential applications in various photonic technologies, including all-optical switching and data processing. Our objective is to calculate the nonlinear optical properties of a range of novel molecular systems. The approach is based on the concept of charge transfer (CT) between donor and acceptor through the thiophene and EDOT oligomer chain. In this research work, first hyperpolarizabilities (β) are calculated using DFT method using B3LYP level and B3PW91 using 6-31G basis set for fourteen thiophene and EDOT derivatives using GAUSSIAN98W. The designing of systems with high charge transfer is key to this part, as intra molecular charge transfer between donor and acceptor will lead to a very large value for β (Table).

All these molecules are equipped with NH_2 and NO_2 groups either side to enhance and direct the electron cloud to polarize in a single direction. Oligothiophenes and oligo EDOTs which are used as organic semiconductor materials show significantly high β values exceeding 1000×10^{-30} esu as the number of thiophene units exceed four. For the molecules a-g as the number of thiophene rings increases the hyperpolarizability (β) values increase exponentially, while the HOMO LUMO energy gaps decrease. However, the hyperpolarizabilities of molecules h-m (k_1 :pentakisEDOT and k_2 :pentakisEDOT ethylhexyl) deviate from the trend observed in oligothiophenes primarily due to the loss of planarity and consequent loss of conjugation of the optimized structures as they possess substituted alkyl groups. Alkyl groups are included in the backbone to improve the solubility which will increase the ability of these materials to be used as thin film materials in electronic devices. Such loss of conjugation disrupts the facile charge transfer (CT) across the overlapped p orbital system reducing the β value significantly. Nevertheless, even with such reductions they show very high first hyperpolarizabilities. These materials show superior NLO properties compared to simple conjugated organic systems. Some of these materials have already been synthesized.

chain. In this research work, first hyperpolarizabilities (β) are calculated using DFT method using B3LYP level and B3PW91 using 6-31G basis set for fourteen thiophene and EDOT derivatives using

Molecule	Hyperpolarizability β (10^{-30} esu)	
	B3LYP/ 6-31G	B3PW91/ 6-31G
a	70.99	71.44
b	256.50	258.27
c	660.43	664.30
d	1352.34	1357.29
e	2344.30	2345.73
f	3605.72	3595.54
g	5126.22	5094.32
h	68.45	68.96
i	247.00	249.19
j	660.10	666.32
k_1	1402.72	1416.26
k_2	1078.54	1086.80
l	1738.73	1751.36
m	2875.60	2901.00

Keywords: Charge transfer, NLO properties, hyperpolarizability, DFT