

BIOINSPIRED MACROMOLECULAR ELECTRETS BASED ON ANTHRANILAMIDE DERIVATIVES

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Polypeptide α -helices possess a considerable intrinsic dipole moment (4 to 5 Debye per residue) that has been demonstrated to cause rectification of charge transfer processes. In α -helices, the intrinsic dipole moment results from the orientation of the amide bonds in an ordered direction and the collective shift in electron density upon formation of an internal network of hydrogen bonds. Therefore, polypeptide helices are a representative example for biological macromolecular electrets. (Electrets are dielectrics that contain permanent electric dipole moments with ordered orientations: i.e., electrets are the electrostatic equivalent of magnets.)

Polypeptide helices, however, mediate charge transfer via tunneling through sigma, hydrogen and amide bonds, which is inefficient for distances beyond 1.5-2nm. Synthetic polymers with narrow band gaps can mediate long-range charge transport. Aromatic poly-ortho-amides have extended π -conjugation along their backbones. These polymers are bioinspired in a sense that their secondary conformation is held together by a network of hydrogen bonds between amide groups with ordered direction. We determined that the codirectional orientation of the amide bonds and the collective shift in electron density, resultant from the hydrogen-bond formation, produces an intrinsic dipole moment that is comparable to that of polypeptide α -helices.

Using ab initio density functional theory calculations, we modeled oligoanthranilamide derivatives with different lengths. All structures were optimized using the B3LYP exchange correlation functional with the 6-311G** basis set. Dependence of the electronic properties of the oligomers on their lengths revealed that each residue contributes about 3 Debye to the macromolecular dipole moment. We observed a good agreement between experimentally determined and calculated dipole moments.

We also investigated n- and p-doping of the oligomers by attaching electron donating and electron withdrawing groups, respectively, to various positions of the aromatic ring of the residues. We observe that: (1) a proper positioning of the electron donating and withdrawing groups further polarizes the aromatic residues, increasing the intrinsic dipole moment to about 5 Debye per residue; and (2) an extension of the π -conjugation by the doping groups narrowed the band gap with as much as 1 eV. We believe that the investigated bioinspired systems offer perspectives for the development of broad range of organic electronic materials with non-linear properties. The expected rectification properties of the oligoanthranilamide present venues for improved photovoltaics and molecular-electronics applications.