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First Principles Nano-engineering of Organic Electro-Optic Materials and Devices

Larry R. Dalton

Department of Chemistry, University of Washington, Seattle, WA 98195-1700
dalton@chem.washington.edu

ABSTRACT

It is well known that the electronic and photonic properties of π-electron organic materials are defined by the intra- and intermolecular positioning of π-orbitals, i.e., the structure and nanoscopic arrangement of molecules or of the π-electron segments of polymers. We have used first principles quantum and statistical mechanical calculations to guide the design of π-electron charge transfer chromophores that assemble under the influence of electrical and optical poling fields into noncentrosymmetric lattices exhibiting extraordinary electro-optic activity, low optical loss, and excellent thermal stability. Currently, electro-optic coefficients relevant to device application at telecommunication wavelengths that are 15 times greater than inorganic crystalline lithium niobate are obtained. Coupled time-dependent density functional theory (TD-DFT) modified to incorporate reaction fields and Monte Carlo (both fully atomistic and pseudo-atomistic)/Molecular Dynamics calculations have been used to simulate the role of intermolecular electrostatic interactions in defining acentric chromophore order and dielectric environment effects on measured electro-optic activity. A new class of nanomaterials, binary chromophore organic glasses (BCOGs), is defined. BCOGs consist of a guest chromophore doped into a chromophore-containing host, which can be a single-chromophore-containing dendrimer, a multi-chromophore-containing dendrimer, a chromophore-containing dendronized polymer, or a chromophore-containing polymer of hyperbranched polymer. Very little spectral line broadening or solvatochromic shifts are observed for such doping in contrast to the behavior observed for doping a chromophore into a traditional polymer. The electric field poling-induced order of guest and host chromophores influence each other and lead to dramatically increased electro-optic activity. This phenomenon is further demonstrated by using laser-assisted poling (LAP) to increased the order of disperse red 1 chromophores existing in a DR1-co-PMMA homopolymer. The LAP-induced increase in order of the DR1 chromophore produces a dramatic increase in the order of a guest charge transfer chromophore doped into the DR1-co-PMMA. First principles simulations of the behavior of a variety of BCOGs are discussed. The incorporation of organic electro-optic materials into silicon photonic nano-slotted (70-100 nm) waveguides is also discussed and shown to lead to low drive voltage, high bandwidth, electro-optic modulation; low optical low (milli-microwatt) optical rectification; and low power, 10 THz all-optical modulation. Nanoscopic control of organic π-electron materials is shown to lead to precise control of intramolecular charge perturbation (critical to large 2nd and 3rd order optical nonlinearities) and control of charge transport (critical to organic electronic, photovoltaic, and photorefractive device performances).