DFT Calculations on the Wavelength Dispersion of Absorbance and Refractive Indices for Molecular Design of Photonic Polymers

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Abstract

Density functional theory (DFT) calculations using the B3LYP hybrid functional and the 6-311++G(d,p) basis set have been performed to predict the wavelength dispersion of optical absorbance and refractive indices for organic compounds and polymers in the range between the vacuum UV (~157 nm) and near-IR (~850 nm). The DFT calculations can reproduce the experimental dispersions of absorbance and refractive indices with high accuracy and low costs.

Introduction

Control of transparency, refractive index, and their wavelength dispersions are indispensable for design of optical/photonic polymers such as for plastic fibers, photo-resists, micro-lens, optical discs, and thin films for flat panel displays. For developing novel optical/photonic polymers, prediction of the wavelength dispersion of absorbabnce and refractive indices is indispensable and strongly required. However, such predictions still rely on empirical rules based on molecular or atomic contributions. For more accurate reproduction of the dispersions, quantum chemical calculations have been performed. However, such calculations do not demonstrate satisfactory performance for quantitative prediction of experimental values.

Methods

The DFT level of theory with the three-parameter Becke-style hybrid functional (B3LYP) was adopted in conjunction with the Gaussian basis sets. The 6-311G(d) basis set was used for geometry optimizations under no constraints, and the 6-311++G(d,p) was used for the calculations of one-electron transition energies, their oscillator strengths, and frequency-dependent polarizabilities. The calculated absorbance was represented by a oscillator strength divided by the van der Waals volume (nm^3) of molecule. For reproducing the shapes of absorption spectra, each calculated transition was replaced by a Gaussian broadening function with a full width at half height of 0.35 eV. The refractive indices and their dispersions were estimated according to the Lorentz-Lorenz equation using computed wavelength-dependent polarizabilities and experimental densities. The software package of Gaussian-03 (Rev.D01) was used for calculations.

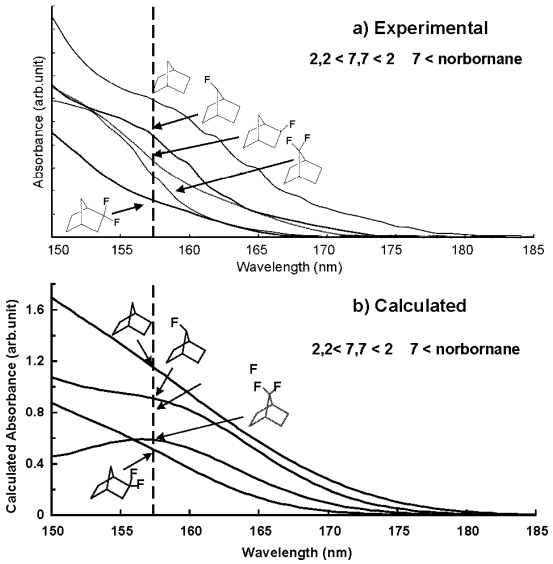

Figure 1. Experimental and calculated spectra of unsubstituted and fluorine-substituted norbornanes. The order of the experimental absorbance at 157 nm is perfectly reproduced by the computation.

Results & Discussion

As shown in Figs.1-3, the DFT calculations can reproduce the dispersions of optical absorbance and refractive indices with high accuracy. The calculated dispersions demonstrate that the judicious introductions of -F and -CF_3 into alicyclic and heterocyclic compounds are effective in reducing the absorption and refractive indices at shorter wavelengths, though small compounds containing bromine and sulfur are slightly deviate from the linearity (Fig.2). In addition, the calculated refractive indices at 589 nm and the Abbe numbers that represent the refractive index dispersion in the visble region agree well with the experimental values. Further, the refractive index dispersion in the deep UV region (157-248 nm) can be well estimated from the calculated Abbe numbers. These results indicate that DFT method is a very useful tool for quantitative prediction of the dispersion of absorption and refractive indices for a wide range of organic compounds and polymers for optical and photonic applications.

Reference

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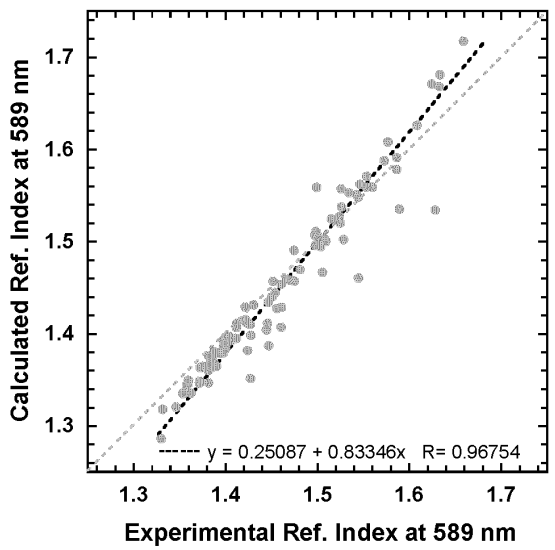

Figure 2. Plots of calculated *vs.* experimental refractive indices at 589 nm for 101 organic compounds. The compounds containing bromine and sulfur are slightly deviate from the linearity.

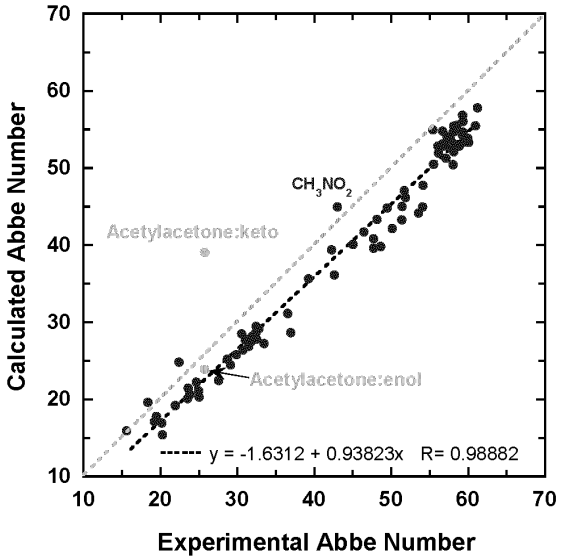

Figure 3. Plots of calculated *vs.* experimental Abbe numbers for 101 organic compounds. The dispersion in the deep UV region also show good correlation with the Abbe numbers.