Reply to "Comment on 'Time-Dependent Density Functional Study of Electroluminescent Polymers'"

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The comment to our previous publication performs calculations for the absorption and emission transition energies of poly(*p*-phenylene vinylene) (PPV) by hybrid B3LYP density functional theory with the 6-31G* basis set on the basis of the geometrical optimizations by SCF, CIS, and B3LYP levels of theory. Most oligomers of the monomer (PPV1) through the decamer (PPV10) have been computed, and polynomial functions up to the sixth degree, as well as multiparameter exponential decay functions, have been utilized to extrapolate the aforementioned transition energies. Various "averaged" structural parameters are additionally displayed in comparison with the experimental values to assist the polynomial-fitted energetic.

It is, in principle, better to calculate more points for extrapolation. Nevertheless, in the studied case, the linearity is quite good; thus, the extension of polymer size from heptamer to decamer does not change the nature of the fit significantly. In addition, although polynomial functions of high degrees perform relatively well for the extrapolation, they exhibit less direct physical insights.[1] The implication of the degrees and the parameters remains uninterpretable.

The geometries optimized by the Hartree−Fock method are known to be relatively inferior compared to theories incorporated with electronic correlations.[2,3] Because the definition of "averaging" was not provided, we are unable to judge if the match between averaged-HF and averaged-experimental values in Table 2 of the comment is merely a coincidence. The claim that HF leads to superior geometry should be justified with more data. It is noticed that the data reported in the comment show that the geometric parameters by different methods actually distribute within the same range. It has been well known that a better comparison with experimental results does not necessarily imply a more reliable choice of computational method because the effect of error cancellation may play a major role and it is difficult to control or predict the error cancellation.

The CIS method in the Gaussian package requires fewer resources to proceed compared to CASSCF in such a large system; however, the CIS method still demands large disk space or becomes extremely time consuming if the in-core computation is carried out.[4] The CIS calculations are not reliable if a small basis set is utilized. In our reported CIS calculation, the optimization for PPV4 ($C_{34}H_{28}$) with the 6-31G* basis set (566 basis functions) required ∼150 GB of scratch storage in a 64-bit Compaq/Alpha system. The optimization for PPV10 ($C_{82}H_{64}$, 1358 basis functions with basis set 6-31G*) reported in the comment would become a benchmark study in the excited states with CIS theory, and the computational information is indeed sufficiently interesting to be reported with details.

The possible negative Stoke shift resulting from linear regression in the studies of polymers was noticed; it is calculated only with many assumptions and is to be used as a quick reference only when the resulting energy is reasonable. Because accurate spectral studies for large molecules using time-dependent DFT excitations have employed ground-state structures optimized with DFT methods[5,6] instead of SCF, proper correction to the Stoke shift should be done in the excited state by more reliable geometrical minimization methods. When the Stoke shift is determined, care must be taken in the excited state as well as the ground state.

References and Notes

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