COMMENTS

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

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To investigate the geometric and electronic structures of poly(*p*-phenylenevinylene) (PPV), many researchers have examined oligo(*p*-phenylenevinylene) (OPV*n*, where *n* is the number of monomers) with defined chain lengths as model compounds for the corresponding monomer and estimated the polymer properties by extrapolation to infinity (Figure 1). In a recent paper, Yu et al.[1] calculated the absorption and emission transition energies at the time-dependent density functional theory (TD-DFT) level. The BP86, BLYP, and B3LYP functionals were employed, and B3LYP gave the best performance. The S_0 structures were fully optimized at the ab initio Hartree−Fock and the B3LYP levels of theory. The CIS approach was employed to determine the S_1 excited-state structures. The reported values were 2.486, 2.231, and 2.008 eV at the TD-B3LYP//HF, TD-B3LYP//B3LYP, and TD-B3LYP//CIS levels of theory, respectively.[1] The authors[1] estimated the absorption and emission energies of PPV from the calculations for OPV1, OPV2, and OPV3 by plotting the corresponding transition energies against the reciprocal of the number of monomer units ($^1/_n$) and by linear extrapolation of *n* to infinity.

However, we note that the OPV3 chain may be too short to give meaningful values for the polymer properties. Although the authors calculated the OPV up to OPV7 at the TD-B3LYP//B3LYP level for the $S_0 \rightarrow S_1$ transition energy and estimated polymer properties using a linear extrapolation,[1] some studies[2,3] have pointed out the shortcomings of such linear extrapolation for the PPV derivatives. The evaluated Stokes shift, defined as TD-B3LYP//B3LYP (S_0) − TD-B3LYP//CIS (S_1), was found to be 0.223 eV in ref 1. However, we wonder if the geometric differences between the B3LYP (S_0) and CIS (S_1) geometries may correctly represent the geometric changes by the $S_0 \rightarrow S_1$ excitation for PPV.

In this comment, we have calculated the absorption ($S_0 \rightarrow S_1$) and emission ($S_1 \rightarrow S_0$) transition energies of PPV to estimate the possible errors in the results of ref 1 caused by the above-mentioned problems. The models from OPV1 to OPV10[4] were calculated using the same method as that in ref 1. Kohn−Sham DFT calculations were performed with the hybrid B3LYP functional. The 6-31G(d) basis set and the "ultrafine" grid were used for the DFT calculations. All calculations were performed using Gaussian 03 programs.[5]

Table 1 lists the absorption ($S_0 \rightarrow S_1$) and emission ($S_1 \rightarrow S_0$) transition energies computed at the TD-B3LYP level of theory. Various functions were employed for estimating extrapolated polymer properties. The extrapolated values vary significantly, by up to 0.39 eV, depending upon the functions employed for extrapolation. In particular, the performance of the linear extrapolations seems to be poor with relatively low r^2 values, implying that the use of a linear function may

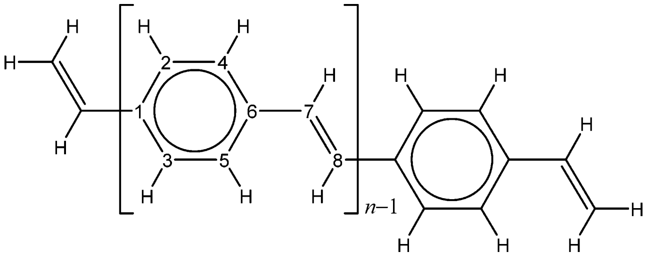

Figure 1. Atomic configurations of oligo(*p*-phenylenevinylene) (OPV*n*, where *n* is the number of monomers).

TABLE 1: Absorption and Emission Transition Energies (in eV) Computed at the TD-B3LYP Level of Theory with the 6-31G(d) Basis Sets[a]

	TD-B3LYP//HF	TD-B3LYP//CIS	TD-B3LYP//B3LYP
polymer units (*n*)	absorption $S_0 \rightarrow S_1$ (*f*)	emission $S_1 \rightarrow S_0$ (*f*)	absorption $S_0 \rightarrow S_1$ (*f*)
1	4.4966 (0.651)	3.9391 (0.717)	4.3475 (0.682)
2	3.5511 (1.572)	3.0140 (1.715)	3.3545 (1.576)
3	3.1207 (2.318)	2.6309 (2.570)	2.8950 (2.365)
4	2.8901 (3.007)	2.4274 (3.338)	2.6408 (3.093)
5	2.7536 (3.661)	2.3159 (3.985)	2.4866 (3.762)
6	2.6662 (4.291)	2.2535 (4.558)	2.3872 (4.396)
8	2.5683 (5.576)	2.1954 (5.578)	2.2726 (5.714)
10	2.5183 (6.904)	2.1752 (6.457)	2.2129 (7.076)
	extrapolated polymer properties		
	*m*th-degree polynomial function[b]		
	$S_0 \rightarrow S_1$ (r^2)	$S_1 \rightarrow S_0$(r^2)	$S_0 \rightarrow S_1$ (r^2)
m = 1	2.3246 (0.99297)	1.9449 (0.99705)	2.0219 (0.99031)
m = 2	2.1954 (0.99932)	1.9076 (0.99770)	1.8537 (0.99956)
m = 3	2.2862 (0.99992)	2.0550 (0.99964)	1.9280 (0.99991)
m = 4	2.3774 (1.00000)	2.2260 (1.00000)	2.0308 (1.00000)
m = 5	2.4346 (1.00000)	2.2691 (1.00000)	2.0946 (1.00000)
m = 6	2.4599 (1.00000)	2.2474 (1.00000)	2.1156 (1.00000)
	m-parameters exponential decay function		
	$S_0 \rightarrow S_1$ (r^2)	$S_1 \rightarrow S_0$(r^2)	$S_0 \rightarrow S_1$ (r^2)
m = 3	2.5513 (0.99777)	2.1946 (0.99872)	2.2465 (0.99763)
m = 5[c]	2.4966 (1.00000)	2.1766 (1.00000)	2.1984 (1.00000)
m = 5[d]	2.4845 (1.00000)	2.1695 (1.00000)	2.1739 (1.00000)
m = 5	2.4738 (1.00000)	2.1671 (1.00000)	2.1592 (1.00000)
m = 7	2.4419 (1.00000)	2.1627 (1.00000)	2.1304 (1.00000)
ref 1[e]	2.486 (0.9955)	2.008 (0.9981)	2.231 (0.9946)
expt[f]	2.45		

[a] These transitions correspond to $^1A_g \rightarrow {}^1B_u$ absorptions and $^1B_u \rightarrow {}^1A_g$ emissions with nonzero oscillator strength (*f*). [b] We estimated the polymer properties by plotting corresponding transition energies against $^1/_n$ and by extrapolating *n* to infinity using the *m*th-degree polynomial functions. (*r* is the correlation coefficient.) [c] Extrapolated values from the calculations OPV1−OPV6. [d] Extrapolated values from the calculations OPV1−OPV8. [e] Extrapolated polymer properties. The details are in the text. [f] Reference 7.

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TABLE 2: Optimized Geometries of OPV10 Computed at the HF (S_0), B3LYP (S_0), and CIS (S_1) Levels of Theory[a]

	HF	B3LYP	CIS	expt[b]
$r(C_4-H)$	1.076	1.088	1.076	1.090
$\angle(C_6-C_7-C_8)$	127.0	127.1	127.0	130
$r(C_3-C_5)$	1.380	1.387	1.376	1.396
$r(C_5-C_6)$	1.394	1.410	1.401	1.408
$r(C_6-C_7)$	1.475	1.460	1.459	1.446
$r(C_7-C_8)$	1.329	1.353	1.341	1.369

[a] Average geometries are listed. [b] Reference 8.

introduce nonsystematic errors. The differences between the results of ref 1 and our best-fit results, using a seven-parameter exponential decay fit, are +0.044, +0.101, and −0.155 eV for the TD-B3LYP//HF, TD-B3LYP//B3LYP, and TD-B3LYP//CIS values, respectively, indicating that there are inconsistent deviations in the results of ref 1. We note that the Stokes shift becomes a negative value of −0.032 eV if the definition employed in ref 1 is applied to our results.

The authors calculated the OPV up to OPV7 at the TD-B3LYP//B3LYP level, and the result of 2.041 eV in ref 1 is similar to our $^1/_n$ linear-extrapolated value of 2.022 eV. The inclusion of data for larger oligomers (OPV8 and OPV10) slightly affects the transition energies by 0.01 to ∼0.04 eV in the results using a five-parameter exponential decay fit, as shown in Table 1. These show that the use of proper functions for the extrapolation may be more important than the use of a large model system.

Table 2 lists the optimized geometries at the HF (S_0), B3LYP (S_0), and CIS (S_1) levels of theory. It has been believed that quinoidal deformation[6] occurs by the $S_0 \rightarrow S_1$ excitation. The HF (S_0) → CIS (S_1) geometric changes describe the situation correctly, such as the lengthening of the C_7-C_8 and C_5-C_6 bonds and the shortening of the C_6-C_7 bond, but this is not the case for B3LYP (S_0) → CIS (S_1) geometric changes. Although the B3LYP geometries may be more accurate than the HF ones, it is reasonable that the Stokes shift should be defined as TD-B3LYP//HF (S_0) − TD-B3LYP//CIS (S_1) in this case for PPV. The resulting Stokes shift is determined to be 0.279 eV from our calculations, which is in strong agreement with the measured experimental data of about 0.31−0.32 eV for the PPV derivatives in solution.[2,3]

References and Notes

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