Chapter 6

Molecular Orbital Theory Predictions for Photophysical Properties of Polymers: Toward Computer-Aided Design of New Luminescent Materials

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Molecular orbital (MO) calculations at the semiempirical quantum chemical level have been utilized to study a number of chromophores and polymer building block model molecules. Various conjugated systems – including poly(phenylene-vinylene) derivatives - are considered for potentially luminescent materials targeted across the visible spectral range. After mapping out the relevant geometries at the ground and corresponding excited states, optical transition (absorption as well as emission) energies and oscillator strengths are estimated. Systematic correlation of these calculated properties with measured ones in known materials may guide designing new advanced polymers.

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[1] Dedicated to Professor Frank E. Karasz for the occasion of his 70th birthday

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Introduction

Polymers for optical-electronic applications *(1-3)* — such as light-emitting diode (PLED) substrates *(4-7)* or polymer lasers *(8, 9)*— are among the most intensively studied new advanced materials. In the past, discovering of promising new candidate structures (like that of F.E. Karasz' classic segmented blue emitting polymers *(10, 11)* whose backbone is shown on Scheme **1a**), and then establishing structure-activity relations as they are systematically varied, required a lot of ingenuity as well as difficult trial-and-error search. Modern theoretical chemical calculation methods have now reached the stage where they can be used on systems of size
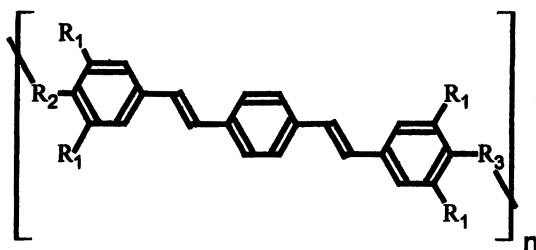
1a: $R_1 = OCH_3$, $R_2 = O$—, $R_3 = O(CH_2)_8$—

1b: $R_1 = H$, $R_2 = $ —, $R_3 = CH=CH$—
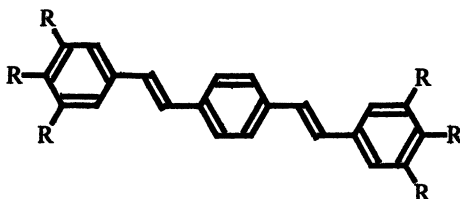
1c: $R = H$

1d: $R = OCH_3$

Scheme 1. Structures of PPV-related polymers and PPV3 model compounds.

relevant to actual applications (i.e. hundreds to thousands of atoms). In this contribution I demonstrate how to utilize these computational techniques in describing photophysical behavior of polymers, in order to aid the design of materials with custom-tailored electronic-optical properties. A few select example molecules are presented, chosen mostly to relate to Karasz's seminal works in the field of poly(phenylene-vinylene) (PPV, Scheme **1b**) based PLED materials *(3)*. Results on these small models (the trimer PPV3 **1c**, and its bis(trimethoxy) substituted analog **1d**) reveal the molecular orbital basis of photophysical behavior in these systems, as will be shown below. In the future we plan larger scale computations that include larger segments containing several of these chromophores, to model interactions in the solid polymer phase between them as well as with the embedding matrix. Calculations of this type may clarify the nature of the photoexcited states and the efficiency of their generation in PLEDs. The discussion here is limited to semiempirical methods (similarly to most reports that have appeared to date *(12)*) which require much less computational effort than do *ab initio* methods, although with the increase of available computing power the later are also beginning to be applicable to medium-sized systems *(13)*.

Computational methods

A computationally efficient combination of various semiempirical quantum chemical methods was used *(12, 14)*, as they are implemented in the MOPAC *(15)* and Arguslab *(16-18)* program packages. All the software runs on commodity personal computers (with AMD Athlon or Intel Pentium class processors). The polymer molecules were modeled with oligomers of sufficient length. For this investigation typically 3-6 repeat units are included in most cases. It has been demonstrated experimentally (e.g. by distyrylbenzenes in relation to PPV-based polymers *(6, 19)*) that in these systems a trimer often exhibits some of the essential features of the extended conjugated polymer already.

The initial geometries for the ground state (S_0) and then for the excited states (singlet S_1 and triplet T_1) were optimized by the semiempirical AM1 method *(14-16, 20)*. All degrees of freedom were fully relaxed with no symmetry or other geometrical constraints applied. The electron spin was restricted according to the state multiplicity (RHF singlet and triplet calculations *(21)*). In the excited states electron correlation was taken into account by using single-excitation configuration interaction for two electrons in two orbitals (the MECI option in the MOPAC program) in these runs. The potential energy minima located were verified by calculating the Hessian force matrix and checking that no imaginary eigenvalues occurred.

At the appropriate points on the potential energy hypersurfaces obtained, the bandgap is estimated as the HOMO-LUMO energy difference, while optical absorption and emission energies are approximated from the distance between the curves forming the Frank-Condon envelope, as illustrated schematically on Figure 1. Spectral intensity is characterized by transition moments and oscillator strengths for the radiative transitions $(^0S_0 \rightarrow ^{FC}S_1, ^0S_1 \rightarrow ^{FC}S_0)$, calculated from a configuration interaction computation (using Slater-type Gaussian orbital base). The INDO1/S-CI Hamiltonian was used in the calculations on electronic transitions (16-18, 22-25). The Einstein-coefficient B_{21} for stimulated emission was also determined, which is useful for judging feasibility of application as a laser substrate. Radiative lifetimes were calculated as well.
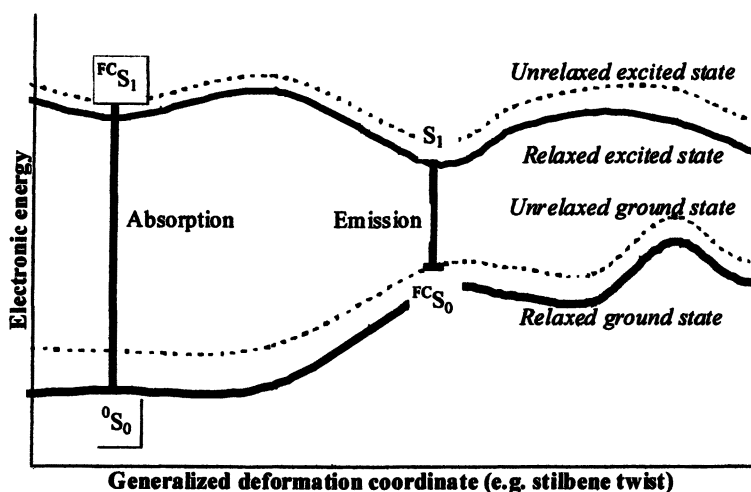

Figure 1. Schematic plot of a cut through potential energy surfaces.

In addition to the above-mentioned static quantities, the dynamics of the evolution of states was also investigated. The dynamic reaction coordinate (DRC) capability of MOPAC, in conjunction with configuration interaction, was used to trace the evolving excited state as it starts from the geometry corresponding to the energy minimum in the ground state. Relaxation following the Frank-Condon vertical transition is simulated in this semiempirical treatment.

Results and discussion

Excited-state molecular dynamics

To illustrate the DRC trajectories calculated, Figures 2a-c show potential energy plots of the S_1 state of 1,4-divinyl-benzene (a model minimal core unit of phenylene-vinylene polymers), evolving from the ground state upon photoexcitation ($^0S_0 \rightarrow ^{FC}S_1$.transition). The zero of the energy scale applied on this figure is set to the initial point reached by the vertical Frank-Condon transition. Different timescale events can be observed over the course of this 4 picosecond simulation. The fastest changes are demonstrated on Figure 2a, with the first 40 fs shown with 0.1 fs calculation timesteps; similar fast modes superimposed on the slower ones are seen at later times as well. The slower changes can be discerned from Figures 2b and 2c, where averages of 20 points (binned over 2 fs) and of 400 points (binned over 40 fs) respectively are plotted to smooth out the rapid oscillations. Since the calculation yields not only the energy, but the coordinates, MO contributions and partial charges of all atoms as well, much theoretical information can be gathered about the relaxing excited state on the femtosecond-picosecond timescale relevant for photophysical processes. For example, the behavior of "breathers" (26) (multi-quanta vibronic states) can be analyzed in extended π–conjugated systems such as PPV-based polymers. Figure 3 illustrates tracing the skeletal motions by displaying the temporal evolution of the C_1-C_2 and C_2-C_3 distances of the phenylene ring in 1,4-divinyl-benzene. The vibronic relaxation of the ground state after $S_1 \rightarrow S_0$ luminescent transition can be studied in the same way.

Conformational mapping of PPV-based polymers

Although their continuous conjugation along the polymer backbone makes these systems stiff, the rather low barrier to rotation around the vinyl-phenyl linkage lends them considerable freedom of movement. The actual extent of this freedom depends on a delicate balance between the tendency of the π–bonding atoms to align co–planarly and the steric hindrance of groups bound to them. It is of interest to map out this conformational behavior theoretically. Semiempirical quantum chemical methods provide a computationally feasible way of calculating a large number of points on the potential energy hypersurface. As a simple example, data on phenylene ring rotation in a methoxy-substituted distyrylbenzene chromophore (Scheme 1d) is presented. This investigation concerned semi-rigid rotation: the terminal phenylene units were held fixed (as if embedded in a very viscous medium), aligned co–planarly with each other; the middle ring was set at certain angles with respect to them, while geometry of the connecting atoms was optimized with these constraints. The ground and excited state potential energy curves so obtained are shown on Figure 4.
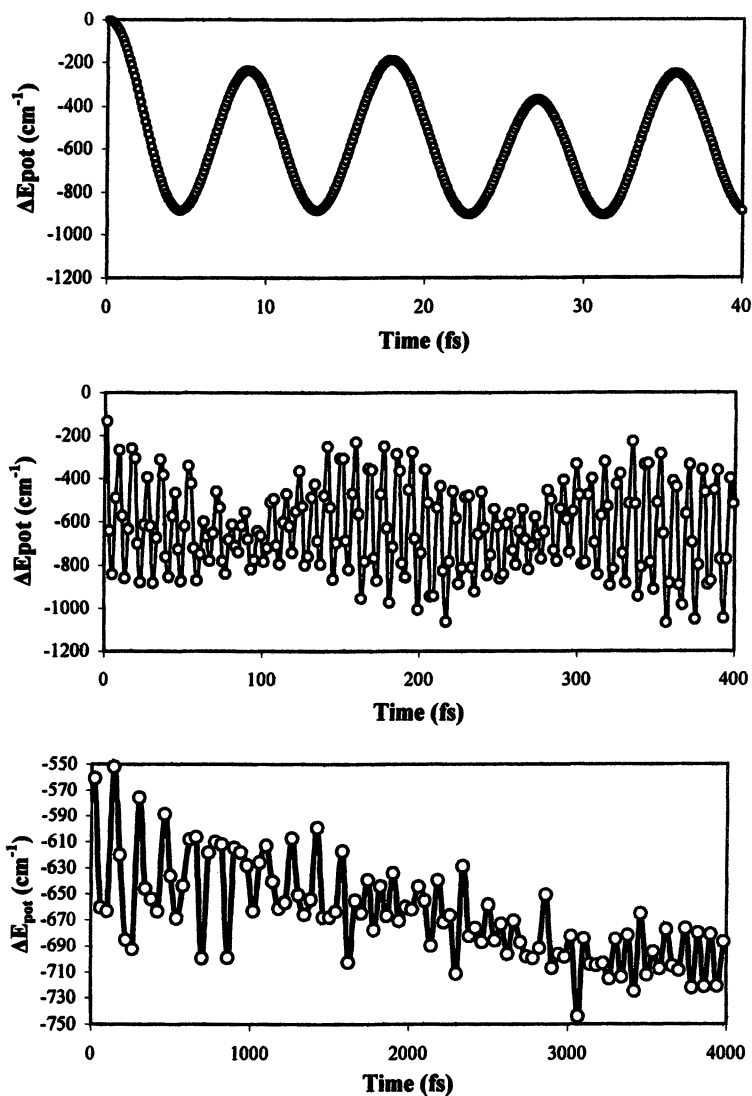
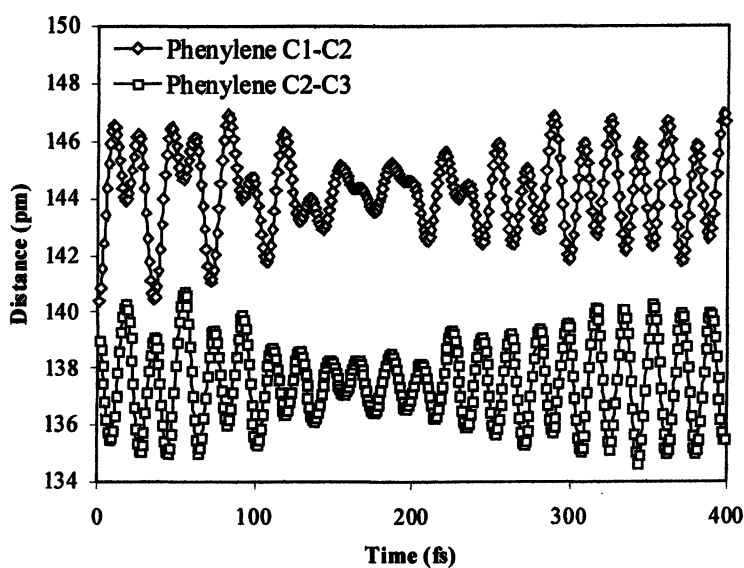*Figure 2a-c. DRC potential energy curves for 1,4-divinylbenzene.*

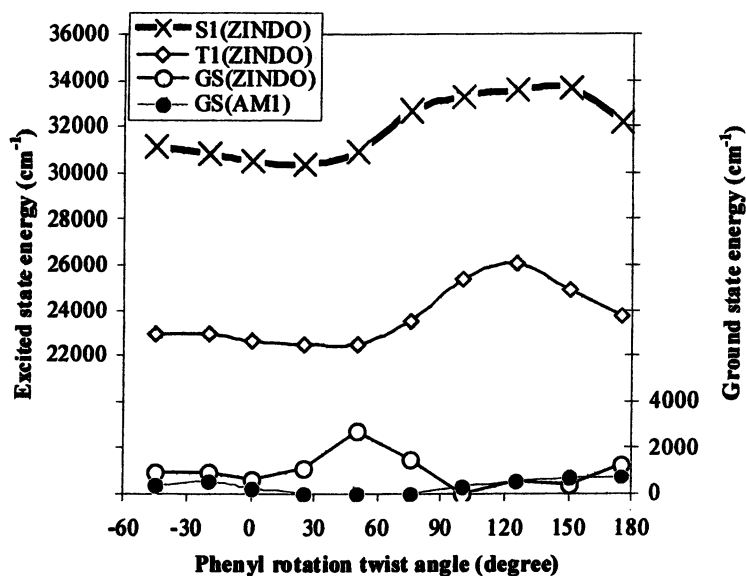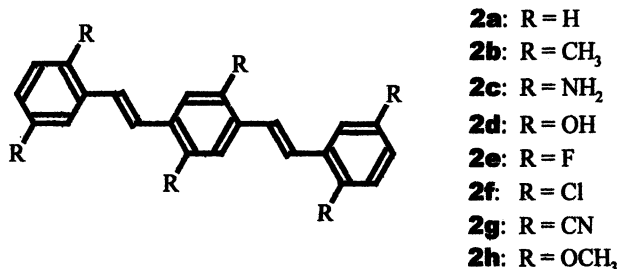*Figure 3. DRC potential energy curves for 1,4-divinylbenzene.*

Figure 4. Potential energy curves for phenylene ring rotation in 1d.

2a: R = H
2b: R = CH₃
2c: R = NH₂
2d: R = OH
2e: R = F
2f: R = Cl
2g: R = CN
2h: R = OCH₃

Scheme 2. Structures of substituted PPV3 model compounds.

Table I. Calculated spectral characteristics of substituted PPV3 molecules

Molecule	λ_a (nm)	f_a	λ_e (nm)	f_e	τ_r (ns)	B_{12} (10^{21} m^3J^1)
2a	334	1.97	379	2.09	1.03	3.18
2b	-27	0.70	3	2.04	1.07	3.12
2c	70	1.64	25	1.64	1.50	2.65
2d	61	1.84	16	1.84	1.27	2.92
2e	-2	1.82	-1	1.95	1.10	2.96
2f	52	1.99	6	1.99	1.12	3.07
2g	77	1.54	31	1.54	1.64	2.53
2h	59	1.82	13	1.82	1.27	2.86

NOTE: transition wavelengths for **2b-h** are shown relative to those of **2a**

Substituent effects on PPV3-based blue-emitting chromophores

A series of 2,5-disubstituted phenylene-vinylene oligomers (Scheme 2) were investigated to reveal systematic trends with varying the substituents. Calculated properties are listed in Table I.

Systematic changes of the absorption and emission wavelengths (λ_a and λ_e) can be seen with varying the substituents, even though the absolute values calculated (shown in the first line of Table I) appear too low.

**Something old, something new – something borrowed, something blue-emitting?**

An obvious advantage of theoretical calculations is that they can be carried out for compounds not yet in existence. Predicted properties can guide selection

3a   **3b**
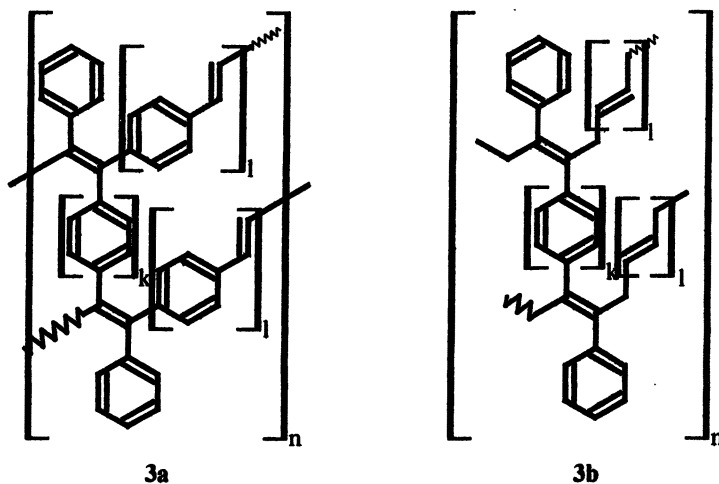
Scheme 3. Structures of crosslinked PV-related polymers and model compounds.

of desirable target molecules to be synthesized. Based on these calculations I propose one interesting new type of polymer[2] (Scheme **3a**), which borrows building blocks from traditional PPV variants, but connects them together in a novel way that may potentially provide for useful luminescent behavior. The chromophore would be the familiar PPV3 trimer segment, but built perpendicularly to the double-stringed backbone. This orientation inhibits energy transfer (since the dipole-dipole overlap is near zero), so that the short segment may be luminescent emitter even in the presence of a longer conjugated segment since it is orthogonal to it. At the same time the uninterrupted conjugation along the backbone provides better carrier mobility than that possible with molecules designed with flexible saturated alkyl spacers. Also the rigid backbone prevents aggregation of the chromophores either with each other or with the backbone. In this respect it resembles ladder-type polymers, but it is more flexible. There is also similarity with the idea of using pendant group chromophores *(7, 27-29)*, but in this case they are held apart at well defined orientations. A variant on this theme is **3b**, which has the simpler polyacetylene backbone instead of a PPV-like one. Calculations are currently in progress for model compounds **4a** and **4b**. As illustrated on Figure 4, displaying the angle between the transition dipole of the intended chromophore and the one polarized along the backbone, there is indeed significant oscillator strength at near-perpendicular direction.

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[2] Actually producing this kind of polymer would likely be difficult, but what would Frank's next seventy year without challenges?

4a

4b
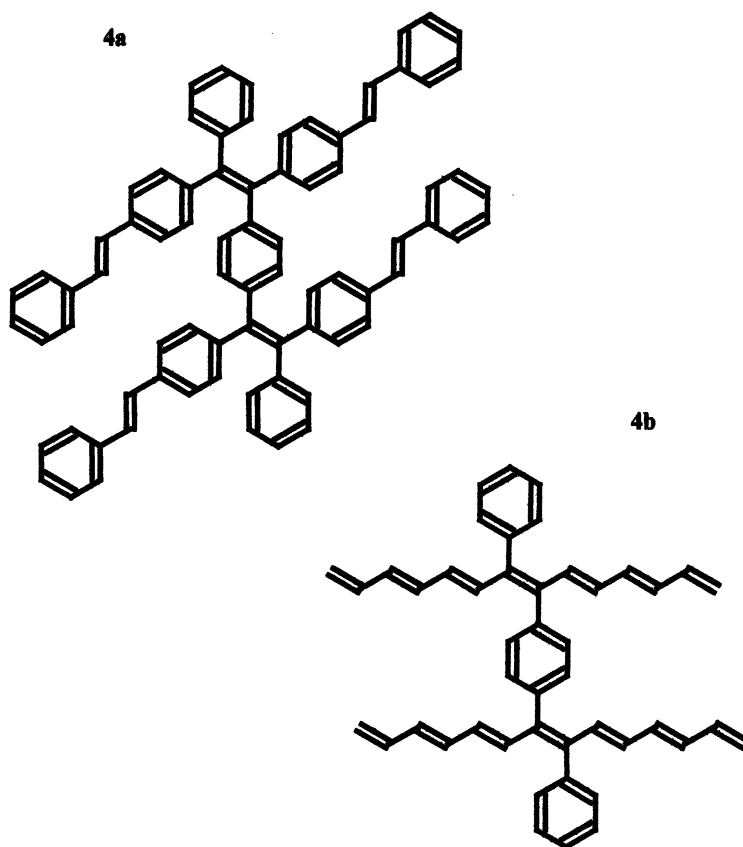
Scheme 4. Structures of model compounds for crosslinked PV-related polymers.
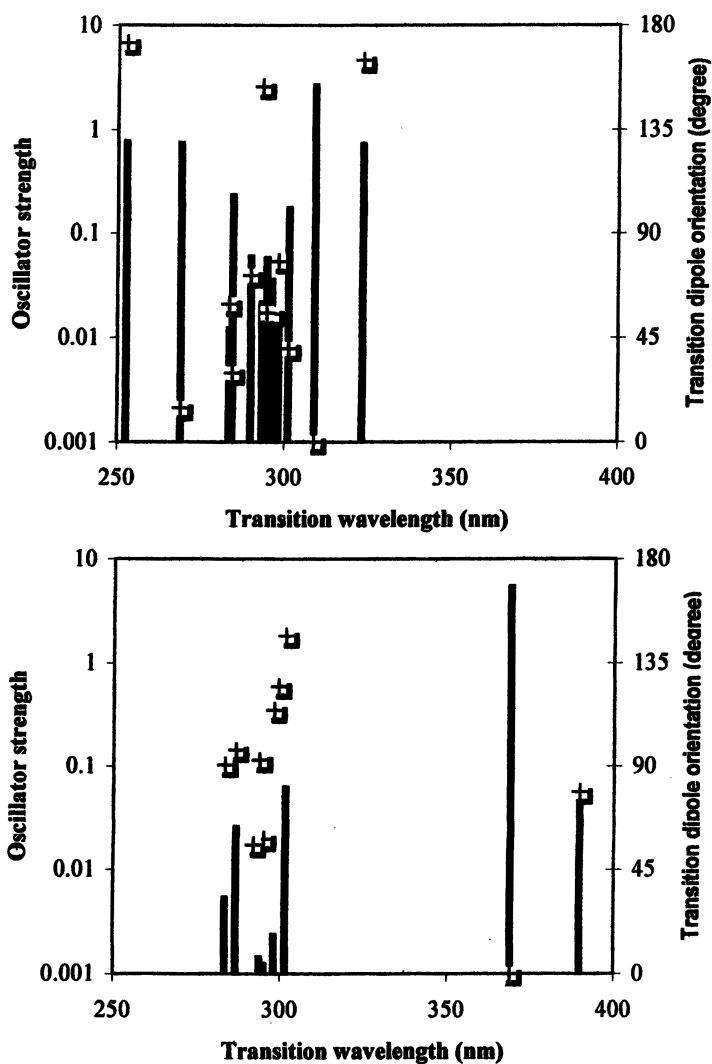
Figure 4. Calculated transitions in crosslinked PV-related polymers *4a* and *4b*.

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