Singlet−Triplet Splittings and Their Relevance to the Spin-Dependent Exciton Formation in Light-Emitting Polymers: An EOM/CCSD Study

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By employing the coupled-cluster equation of motion method (EOM/CCSD) for excited-state structures, we have investigated the structure dependence of the singlet and triplet exciton splittings, through extensive calculations for polythiophene (PT), poly(3,4-ethylenedioxythiophene) (PEDOT), poly(thienylenevinylene) (PTV), polyparaphenylene vinylene (PPV), MEHPPV, polyparaphenylene ethylene (PPE), polyfluorene (PFO), and ladder-type polyparaphenylene (mLPPP). The results for the polymer are extrapolated through computations for the oligomers with increasing length. Recent investigations have been quite controversial about whether the internal quantum efficiency of electroluminescence could be higher than the 25% spin statistics limit or not in polymeric materials. Using a simple relationship between the exciton formation rate and the excitation energy level, we have discussed the material-dependent ratios of singlet and triplet exciton formation, which are in good agreement with the magnetic-field resonance detected transient spectroscopy measurement by Wohlgenannt et al. for a series of electronic polymers. This provides another piece of evidence to support the view that the internal quantum efficiency for conjugated polymers can exceed the 25% limit.

I. Introduction

Since the pioneering discover of polymer light-emitting diodes (LEDs) by Burroughes et al. in 1990,[1] many progresses have been achieved in improving efficiency and stability. In the LED devices, the electrons and holes are injected into the active polymer layer, forming excitons through Coulomb interaction. The radiative decay of excitons emits light. From spin statistics, the injected electrons and holes would form 25% singlet and 75% triplet excitons. In pure organic conjugated polymers, only a singlet exciton can decay radiatively in general. There is great interest in the singlet and triplet exciton structures in the light-emitting materials.

It has been generally believed that the electroluminescence (EL) quantum efficiency is limited to 25% of that of photoluminescence (PL). Indeed, from a study in organic LED Alq_3, Baldo et al. found that the singlet fraction is about 22%.[2] However, by improving the electron transport in PPV films, Cao et al. found that the ratio of EL with respect to PL can reach as high as 50%, which indicates the possibility that the singlet exciton formation rates can be much higher than the triplet excitons.[3] Indeed, Ho et al. confirmed this finding by improving the interface at the molecular level and estimated that the ratio of singlet with respect to triplet is about 45%.[4] Furthermore, Wohlgenannt et al. have designed an experimental scheme by using photoinduced absorption (PA) and PA-detected magnetic resonance (PADMR), which can measure the spin-dependent exciton formation rates directly. They conclude that the singlet over triplet ratio (i) is dependent on materials[5] and (ii) is almost linearly dependent on the conjugation length.[6] Wilson et al. have shown that in the Pt-containing polymer the singlet−triplet exciton ratio can be as high as 57%, whereas for the monomer of the same system, the ratio is a bit less than 25%:[7] these ratios are independent of the temperature, field strength, and film thickness.

The underlying mechanism of the spin-dependent exciton formation rates is far from conclusive. Theoretically, Shuai et al. have first suggested that exciton formation rates are different for different spin manifolds.[8] They pointed out that both off-diagonal interchain correlation and electron−phonon coupling (exciton-binding energy dissipation process) are important for the exciton formation to be spin-dependent. Kobrak and Bittner have applied a mixed quantum classical molecular dynamics approach to simulate the formation process of an electron−hole pair to exciton. They found that the formation rates can be higher for the singlet state than for the triplet.[9] Later, Karabunarliev and Bittner have further explored this mechanism and found that the formation rate can be simply expressed as inversely proportional to the exciton binding energy.[10] Hong and Meng have employed a very different mechanism, the "phonon-bottleneck" formed by a large separation between T_1 and T_2,[11] which largely reduces the internal conversion from T_2 to T_1, and eventually there are more and more T_2 go to S_1, instead of going to T_1. Namely, this ratio is very sensitive to the low-lying triplet state structure. Beljonne et al. have performed correlated quantum-chemical calculations that account for both the electronic couplings and the energetics of the charge-recombination process from a pair of positive and negative polarons into singlet and triplet excitons.[12] In small molecules, the energy difference between the lowest intermolecular charge-separated state and the S_1 exciton state is large, whereas the energy difference becomes on the same order of magnitude as the reorganization energy in extended conjugated chains. They show that the formation rates for singlet over triplet excitons vary with chain length and favor singlet excitons in longer chains. Thus, the resulting singlet/triplet fraction can significantly exceed the spin-statistical limit. Recent investiga-

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tions by Wohlgenannt and Mermer[13] and Barford[14] are in the same line and are consistent with this conclusion.

Note that, in general, theory postulates that the injected carriers form an intermediate interchain of loosely bound pairs that possess definite spin but can convert mutually quite easily through spin−lattice relaxation,[12−16] and the exciton formation process is much slower than that. Indeed, Kadashchuk et al.[17] have measured and calculated the energy splitting between the singlet and triplet states of the interchain polaron pairs (PP), which is found to be very small, lower than kT. Thus, the spin statistics is biased in favor of singlet neutral excitons if the singlet can form with a larger rate than the triplet. However, a recent measurement by Reufer et al. indicates that all the time during carrier capture processes the exchange splitting stays to be substantial, and the singlet yields cannot exceed the 25% limit.[18] Earlier, Segal et al. have questioned the view of spin-dependent exciton formation, and they found that even in conjugated polymer the singlet and triplet formation rates are the same within the experimental errors, thus excluding the possibility of bigger than 25% internal quantum efficiency.[15]

Thus, by and large, whether the internal quantum efficiency for polymer electroluminescence can exceed the 25% limit is still in debate. We note that Meulenkamp et al. have reported that by applying a novel hole injection layer the PLED internal quantum efficiency can be improved to be 60%.[19] This is the first direct evidence based on a device experiment showing that the 25% spin statistics limit can be exceeded. In this work, we report our recent investigations on the material dependence of singlet−triplet splitting, which is closely related to this ratio. We show that the theoretically obtained dependence is in agreement with the spectral measurement by Wohlgenannt et al.,[5] who have attributed the material dependence as originated from the effective bond alternation parameter, δ. Here, we consider the real material structures of the conjugated polymers and we employ the coupled-cluster equation of motion[20] with INDO parametrizations[21] to calculate the excited-state energies for various electronic polymers. The singlet over triplet exciton formation rates are obtained through a simple assumption postulated previously.[10,16] The results contribute to a better understanding of this controversial issue.

II. Theoretical Methodology

The electronic polymers considered in this work are polythiophene (PT), poly(3,4-ethylenedioxythiophene) (PEDOT), poly(thienylenevinylene) (PTV), polyparaphenylene vinylene (PPV), MEHPPV, polyparaphenylene ethylene (PPE), polyfluorene (PFO), and ladder-type polyparaphenylene (mLPPP). The geometric structures for these polymers are depicted in Figure 1. We are mostly interested in their low-lying excited states, which rely heavily on the treatment of the electron correlation effect. In this work, we apply the coupled-cluster single-double equation of motion approach (CCSD-EOM) implemented by the authors[22] with the semiempirical INDO parametrizations. The Ohno−Klopman potential[23] is used to describe the Coulomb repulsion term. Further, we only keep the π-conjugated molecular orbitals in the active space so that we can calculate the excited states for relative long system, that is, about 50 π orbitals with very high precision. Thus, we adopt an oligomer approach, namely, we start with the polymer unit cell, from 2 to 5 repeat units and eventually make extrapolation to the polymer limits. We have optimized the chemical structures of the oligomers by the semiempirical AM1 (Austin Model 1) method implemented in the AMPAC package.[24] In all cases, we assume coplanar conformations that are imposed by π

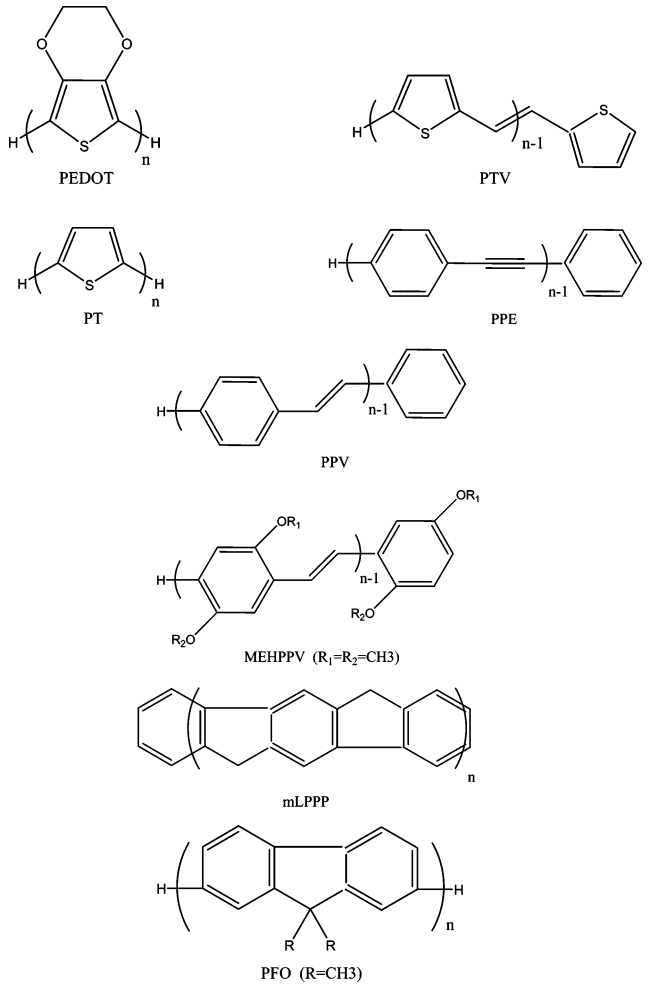

Figure 1. Chemical structures of PEDOT, PTV, PT, MEHPPV, PPV, PPE, mLPPP, and PFO.

delocalization and crystal packing in the films. Then the optimized structures are used in the CCSD-EOM calculations.

We focus on the internal formation process, from a free charge pair into the lowest ionic exciton states, in both singlet and triplet manifolds. Here, the ionic exciton can be identified as the lowest excited state with important contribution from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) excitation. In fact, the initial state, the injected electron and hole loosely bound pair, can be considered as charge excitation. When forming a bound pair, the exciton will keep the ionic character. From the molecular orbital point of view, the HOMO represents the hole orbital and the LUMO represents the electron. Thus, a state that mostly consists of HOMO to LUMO excitation is of ionic nature.

From a time-dependent first-order perturbation, or the Fermi Golden Rule, the formation probability from an initial state (the free charge pair) to a final state (the bound ionic exciton) can be expressed as

$$p = \left| \frac{\langle \mathrm{i}|H'|\mathrm{f}\rangle \sin(\omega_{\mathrm{fi}} t/2)}{E_{\mathrm{i}} - E_{\mathrm{f}}} \right|^2 \tag{1}$$

where p represents the exciton formation probability. The formation rate is the time derivative of the above quantity

$$\sigma = \frac{\mathrm{d}p}{\mathrm{d}t} = \frac{|\langle \mathrm{i}|H'|\mathrm{f}\rangle|^2 \sin(\omega_{\mathrm{fi}} t)}{2\hbar E_{\mathrm{fi}}} \tag{2}$$

TABLE 1: Singlet and Triplet Excitation Energies (in eV) for the Oligomers and Polymers[a]

PEDOT	calcd (S)	exptl (S)	calcd (T)	exptl (T)	MEHPPV	calcd (S)	exptl (S)	calcd (T)	exptl (T)
$n = 2$	3.83	3.87[b]	1.56		$n = 2$	4.08		2.74	
$n = 3$	3.28	3.10[b]	1.27		$n = 3$	3.61		2.52	
$n = 4$	2.97		1.13		$n = 4$	3.34		2.33	
$n = 5$	2.78		1.05		$n = 5$	3.25		2.17	
$n = \infty$	2.09	1.60[c]	0.70		$n = \infty$	2.66	2.48[i]	1.85	1.30[i]
PTV					PPV				
$n = 2$	3.79	3.45[d]	1.69	1.52[d]	$n = 2$	4.48	4.01[j]	2.40	2.13[l]
$n = 3$	3.25	2.85[d]	1.39	1.32[d]	$n = 3$	3.83	3.44[j]	2.37	
$n = 4$	3.00	2.56[d]	1.27	1.23[d]	$n = 4$	3.61	3.20[j]	2.23	
$n = 5$	2.87		1.25		$n = 5$	3.51	3.07[j]	2.17	
$n = \infty$	2.24	1.80[e]	0.91		$n = \infty$	2.80	2.45[k]	2.05	
PT					PPE				
$n = 2$	4.04	4.05[f]	1.85	2.23[g]	$n = 2$	4.83		3.29	
$n = 3$	3.55	3.49[f]	1.52	1.93[g]	$n = 3$	4.28		3.26	
$n = 4$	3.28	3.16[f]	1.36	1.81[g]	$n = 4$	4.03		3.11	
$n = 5$	3.09	2.99[f]	1.27	1.72[g]	$n = 5$	3.90		3.05	
$n = \infty$	2.48	2.20[h]	0.89		$n = \infty$	3.26	3.20[m]	2.92	
mLPPP					PFO				
$n = 2$	3.88	3.30[n]	2.64	2.23[o]	$n = 2$	4.13		2.77	
$n = 3$	3.72		2.57		$n = 3$	3.88	3.56[q]	2.66	
$n = 4$	3.56		2.52		$n = 4$	3.77	3.43[q]	2.56	
$n = 5$					$n = 5$				
$n = \infty$	3.27	2.72[p]	2.41	2.08[p]	$n = \infty$	3.40	3.22[i]	2.36	2.30[i]

[a] Column 1 indicates the oligomers ($n = 2, 3, 4, 5$) and the polymers ($n = \infty$) for different materials. The calculated singlet and triplet excitation energies through INDO/CCSD-EOM for the oligomers and polymers are listed in columns 2 and 4, respectively. The available experimental singlet and triplet values are listed in columns 3 and 5 for comparison. [b] Reference 33. [c] Reference 34. [d] Reference 36a. [e] Reference 36b. [f] Reference 37a. [g] Reference 37b. [h] Reference 38. [i] Reference 29. [j] Reference 39a. [k] Reference 39b. [l] Reference 39c. [m] Reference 41. [n] Reference 42a. [o] Reference 42b. [p] Reference 42c. [q] Reference 43.

H' is the perturbation operator; $|i\rangle$ is the initial state (the free charge pair), and $|f\rangle$ is the final state (the bound ionic exciton); E_i (E_f) is the energy of the initial (final) state while ω_{fi} is equal to $(E_f - E_i)/\hbar$. In fact, the denominator is simply the exciton binding energy. This approach has been employed to investigate the field dependence of the exciton formation rate.[25] The center of interest in this work is to calculate and identify the lowest *ionic* singlet and triplet exciton states (the final state in the above expression). The initial state, namely, the band-edge continuum state, is very difficult to obtain theoretically, and it consists of the most hotly debated subject during the past decade.[26] Recent calculations based on first-principles DFT quasi-particle and particle-hole excitation pictures showed that morphology and interchain arrangements/interactions strongly influence the determination of the exciton binding energy.[27] Here, we simply assume a constant singlet exciton binding energy, $E_b^S = 0.5$ eV for all of the polymeric materials investigated in this work regardless of the disagreement both in theory and in experiment. Then it simplifies our problem to determine the ionic singlet and triplet exciton energy splitting. Finally, by following Karabunarliev and Bittner,[10] the ratio $r_{S/T}$ of the formation rates of the singlet and triplet is

$$r_{S/T} = \frac{\sigma_S}{\sigma_T} = \frac{E_b^T}{E_b^S} = \frac{E_b^S + \Delta_{ST}}{E_b^S} = 1 + 2\Delta_{ST} \qquad (3)$$

where σ_S (σ_T) represents the formation rate of singlet (triplet) exciton, $E_b^{S/T}$ is the binding energy of the singlet/triplet exciton, respectively, and Δ_{ST} is the ionic singlet and triplet exciton energy splitting.

Note that the singlet and triplet exciton energy splitting is also an unsolved problem for electronic polymers. Because the direct observation of phosphorescence in organic polymers is difficult, the determination for the triplet-state structure has been under scrutiny recently. Köhler et al. have argued that there is a universal behavior that for conjugated polymers the exchange energy (the singlet−triplet splitting) is around 0.6−0.7 eV.[28] Monkman and co-workers have measured the triplet energies in a broad range of different conjugated polymers using pulse radiolysis. They found that the singlet−triplet splittings range from 0.6 to 1 eV.[29]

Like the exciton binding energy (E_b), the singlet−triplet splitting (Δ_{ST}) is also a purely electron correlation effect. Even though they have the same origin, they are different in terms of solid-state polarization influence: E_b is dependent on the charge-separated state, which is very much sensitive to the solid-state effects; whereas for Δ_{ST}, both singlet and triplet exciton have a confined spatial extension, thus they are less sensitive to the aggregation effects.

The coupled-cluster (CC) equation of motion approach is so far the most reliable method to determine the excited-state structures. It has been developed to calculate the excited states of π-conjugated molecules and their nonlinear optical response,[30] and the electronic couplings for the singlet and triplet exciton formations.[31] The coupled-cluster method is based on an exponential Ansatz for the correlated ground state. The Heisenberg equation of motion is then constructed based on the CC ground state and its evolution in the single and double excitation configuration space. We have coupled this method with the INDO Hamiltonian in order to have the capability of dealing with relatively large systems with reasonable parametrization. Our previous work showed that this is a reliable and feasible approach for the correlated electrons in conjugated polymers.[22]

III. Results and Discussion

The lowest ionic singlet and triplet excitation energies of the oligomers calculated by INDO/CCSD-EOM and the extrapolated excitation energies for the corresponding polymers are presented in Table 1. The excitation energies for the polymers are obtained by extrapolating the excitation energies of dimers through

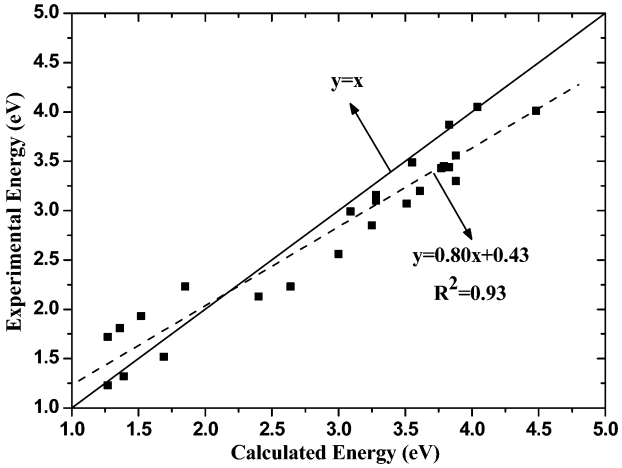

Figure 2. Comparison between the calculated singlet and triplet excitation energies and the available experimental values for the oligomers. The solid line indicates an ideal 1.0 correlation between the calculated and the experimental values. The dashed line is linear regression with the formula and fit given.

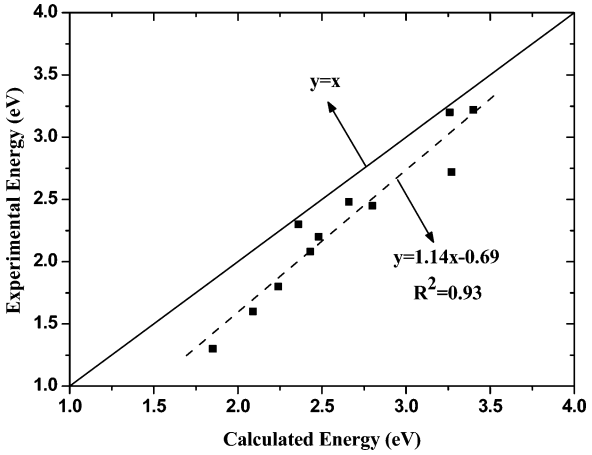

Figure 3. Comparison between the calculated singlet and triplet excitation energies and the available experimental values for the polymers. The solid line indicates an ideal 1.0 correlation between the calculated and experimental values. The dashed line is linear regression with the formula and fit given.

pentamers to infinite chain length. Compared with the available experimental excitation energies for the oligomers, the average deviation of the calculated values is 0.29 eV, while the average absolute error of first-principles time-dependent DFT is about 0.47 eV for conjugated systems.[32] A good linear relationship exists between the calculated excitation energies, and the experimental values for the oligomers as shown in Figure 2. As for the polymers, the extrapolated excitation energies are systematically overestimated, with a slightly larger average deviation of about 0.32 eV. However, the ordering of the singlet excitation energies for the polymers, namely, PEDOT < PTV < PT < MEHPPV < PPV < PPE < mLPPP < PFO, is reproduced well by our computations. The linear relationship between the extrapolated excitation energies and the experimental values for the polymers is also quite reasonable, which is shown in Figure 3.

In the following, we will discuss the excitation energies in detail for all of the conjugated systems shown in Figure 1. The polymers are divided into three types according to the similarity of their chemical structures.

PEDOT, PTV and PT. These three polymers contain the same component, the ring of thiophene, in the main chain, as presented in Figure 1.

(i) PEDOT is highly electron-rich due to the alkylenedioxy substituents on the rings of thiophene.[33] The optical band gap for PEDOT is measured to be 1.6 eV.[34] For the dimer and trimer of PEDOT, the calculated singlet excitation energies are 3.83 and 3.28 eV, respectively, which agree very well with the available experimental values of 3.87 and 3.10 eV,[33] see Table 1.

(ii) PTV has a greater extent of π conjugation with the insertion of double-bond linkages in the backbone, which reduce the steric interactions on successive aromatic rings and increase the degree of coplanarity of the conjugated polymer backbone. The singlet excitation energies for the oligomers of PTV are reduced with respect to the corresponding oligomers of PT. The extrapolated singlet excitation energy for PTV is about 0.24 eV lower than that of PT, due to the presence of the double-bond linkages. Similar results have been found previously.[35] As shown in Table 1, the calculated excitation energies for the oligomers of PTV are in agreement with the experimental values.[36]

(iii) As for PT, the calculated singlet excitation energies of the polymer and its oligomers agree well with the experimental values.[37] However, the triplet excitation energies[38] are underestimated by about 0.5 eV, which may be attributed to the coplanar geometry assumed in the calculation. Both theory and experiment have shown that the oligomers of PT are not planar but subject to a strong rotational disorder.[37b]

MEHPPV, PPV and PPE. MEHPPV is PPV substituted with alkoxy chains on the phenyl rings, while PPE has triple-bond linkages in place of double-bond linkages in PPV, as depicted in Figure 1.

(i) The long alkoxy chains in MEHPPV are modeled by the short chains of methoxy for the simplicity of computation. For MEHPPV, the calculated singlet excitation energy of 2.66 eV agrees with the experimental value of 2.48 eV.[29]

(ii) Compared with the experimental values,[39] the calculated singlet excitation energies of PPV and its oligomers are systematically overestimated by about 0.4 eV. The calculated singlet−triplet energy splitting of 0.75 eV for PPV is consistent with other theoretical results.[28c,40]

(iii) For PPE, the calculated singlet excitation energy of 3.26 eV is in good agreement with the experimental value of 3.20 eV.[41] PPE is found to have the smallest singlet−triplet splitting of 0.34 eV among all of the polymers from our calculations.

mLPPP and PFO. Compared to poly(p-phenylene) (PPP), both mLPPP and PFO are stabilized of the backbone chain against torsional displacement of the phenyl rings by covalent bridging.

(i) For the dimer and polymer of mLPPP, the correspondence between the theoretical singlet and triplet excitation energies and the experimental values[42] is a bit poorer than that for other molecules, see Table 1: we have neglected all of the alkyl chains in the computations. The calculated singlet and triplet exciton energy splitting is 0.86 eV for mLPPP, which is consistent with the singlet−triplet splitting of 5000 cm^{-1} (0.62 eV) obtained from the fluorescence and phosphorescence spectra for the polymer.[42b]

(ii) For the trimer and tetramer of PFO, the calculated singlet excitation energies agree well with the experimental values,[43] as shown in Table 1. For the polymer, the calculated singlet and triplet exciton energies are 3.40 and 2.36 eV, respectively, in excellent agreement with the experimental values of 3.22 and 2.30 eV.[29]

According to the simple eq 3, the ratios $r_{S/T}$ of the singlet and triplet exciton formation rates for the materials investigated in this work can be obtained from the extrapolated singlet and

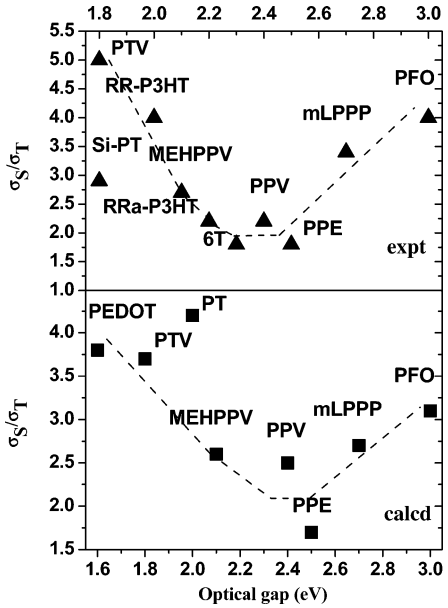

Figure 4. Comparison between the experimental (expt) and calculated (calcd) results of the ratios of singlet and triplet exciton formation rates as a function of the optical gaps for different polymers. The dashed lines are guides to the eye.

TABLE 2: Comparison Between the Calculated and Experimental of Wohlgenannt et al.[5] on the Ratios of the Singlet and Triplet Exciton Formation Rates for Electronic Polymers

polymer	PEDOT	PTV	PT	MEHPPV	PPV	PPE	mLPPP	PFO
calcd	3.8	3.7	4.2	2.6	2.5	1.7	2.7	3.1
exptl		5	4	2.7	2.2	1.8	3.4	4

triplet excitation energies. The calculated ratios as well as the experimental values[5] are represented in Table 2. For the sake of clarity, we depict the results in Figure 4. The overall trend of the material dependence of the ratios of singlet and triplet exciton formation rates is reproduced well by our calculations. This agreement independently provides evidence to support the experiment by Wohlgenannt et al.,[5] which has been questioned by several measurements.[15,18] For all of the materials, the calculated ratios $r_{S/T}$ are larger than 1, which indicates that the possibility of polymer EL internal quantum efficiency can exceed the 25% spin statistics limit.

IV. Summary

To summarize, we have employed the INDO/EOM-CCSD approach to calculate the ionic singlet and triplet excitation energies for oligomers of PEDOT, PTV, PT, MEHPPV, PPV, PPE, mLPPP, and PFO. The obtained excitation energies for both oligomers and polymers (through extrapolation) are in agreement with the available experiments, with average deviations of 0.29 and 0.32 eV for oligomers and polymers, respectively. From a simple model postulated previously[10,16] in eq 3, we have estimated the ratios of singlet and triplet exciton formation rates by assuming a universal singlet exciton binding energy of 0.5 eV for all of the polymers. Our theoretical results for the singlet and triplet splittings in electronic polymers as well as the material-dependent ratios of singlet and triplet exciton formation rates are in good agreement with the experiments. This provides independent evidence to support the view that the internal quantum efficiency can exceed the 25% spin statistics limit. It also provides very useful guidance for designing light-emitting polymers with high EL quantum efficiency.

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