Comprehensive Investigation of the Photophysical Behavior of Oligopolyfurans

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The photophysical properties of (oligo)polyfurans (Fn, where $n = 1-5$ represents the number of rings) are presented for the first time for 2−4 rings and compared to parallel data for the corresponding (oligo)-polythiophenes (Tn). The quantum yields of fluorescence of the polyfurans are consistently considerably greater (5−50-fold), and that of the triplet occupation, considerably smaller (2.5−4) than for the polythiophenes. The k_F of the Fn set vary from about equal ($n = 4$) to ≈4-fold greater ($n = 2$) than for the Tn set. The k_{ISC} of the Fn set are from 10−25-fold smaller than for the Tn set. The Fn set shows very little internal conversion (except some for F2) and less than for the Tn set. Triplet lifetimes of the Fn set are ≈3 fold less than for the Tn set. The lowest excited singlet state of the polyfurans is of ^1B_u (or $^1B_1$) character and not ^1A_g. The magnitude of the intersystem crossing is essentially constant as a function of n for the Fn set whereas there is a large decrease for the Tn set as n increases. This indicates a difference in the mechanism for intersystem crossing as is discussed. The π-delocalization is greater for the Tn set than for the Fn set. It is not possible to clearly distinguish whether cis and trans conformers simultaneously exist (most likely for F2), or the magnitude of inter-ring bond twisting but the latter appears to be no more than 20−30 degrees and the virtual molecules at 77 K are clearly more planar than at room temperature.

Introduction

There have been several studies on the photophysics of oligothiophenes in solution, for example, see refs 1−11. However, we are not aware of any photophysical/photochemical studies on the oligopolyfurans
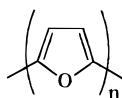
or mixed furan−thiophene−pyrrole oligomers which we shall consider in another paper.

There is some very limited absorption data on some of the oligopolyfurans and mixed oligomers, for example, refs 12−13. Significant interest has been expressed in the oligopoly-thiophenes in relation to their applications in molecular electronics.[14]

In this paper we shall compare the oligopolyfurans (Fn) with the oligopolythiophenes (Tn) for $n = 2, 3, 4$ with respect to geometry, electronic delocalization, spin−orbital coupling, and the major photophysical properties (emission spectra, fluorescence quantum yields ϕ_F, triplet quantum yields ϕ_T, emission lifetimes and all the decay rate constants of the lowest excited singlet state k_F, k_{IC}, k_{ISC}). In addition, we shall compare the singlet, $S_0 \rightarrow S_1$ and triplet, $T_1 \rightarrow T_n$ absorption spectra and extrapolate/predict singlet and triplet absorption data.

The problem of a distortion of the rings in the oligofurans has been considered both at a theoretical as well as experimental level.[15−17] Based on ^{1}HNMR[15] data in a liquid crystal,[15] it was concluded that for F2, the trans form was more stable than the cis and that the trans dominated over the cis. Other solution data based on IR and Raman studies suggested that for F2, the cis was more stable than the trans and that both were twisted.[16] Another theoretical study[17] suggested that all of the Fn were coplanar and that for F2, the cis was more stable than the trans. In this work, theoretical data will be compared with experimental absorption data and we shall examine possible conformations in solution.

Experimental Section

The compounds were synthesized following the procedure in the literature.[18] The yields we obtained were similar and the NMR supported the structure of the compounds $n = 2, 3, 4$.

All the used solvents were of spectroscopic or equivalent gade. Ethanol was kept dried by refluxing over CaO. The solutions used ($10^{-6}-10^{-5}$ M) were deoxygenated by either nitrogen or argon bubbling.

Absorption and fluorescence spectra were run with a Shimadzu 2100 and a SPEX Fluorog spectrometer, respectively. All emission spectra were corrected for the wavelength response of the system.

The fluorescence quantum yields at 293 K were measured using several standards,[1] namely bithiophene ($\phi_F = 0.013$ in acetonitrile), terthiophene ($\phi_F = 0.056$ in acetonitrile), and quaterthiophene ($\phi_F = 0.16$ in acetonitrile).[1] The fluorescence quantum yields at 77 K were obtained by running under the same experimental conditions the solution done at 293 K,

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TABLE 1: Absorption and Photophysical Properties of the Polyfurans and Polythiophenes in Acetonitrile

compound	F1	T1	F2	T2	F3	T3	F4	T4	F5	T5
λ_{max}(abs)	209	231	282	303	328	351	361	392	382 (P)[a]	413
ϵ_{max} (M⁻¹ cm⁻¹)	7600		19150	12400	28700	24215	28600	34700		42700
λ_{max}(fluor)			298, 313[d]	360	352, 371[d]	405, 422[d]	391, 413[d]	445, 474[d]		479,[d] 511
ϕ_F			0.51	0.013	0.74	0.056	0.79	0.16		0.33
τ_F/ns			0.91	≤0.1	1.56	0.18	1.74	0.48		0.90
ϕ_T			0.24[b]	0.93	0.31	0.90	0.29	0.71		0.63
τ_T (μs)			39, 102[b]	124, 146,[b] 104[c]	13, 34[c]	62, 108,[b] 88[c]	14	40, 48,[b] 38[c]		20
k_F (ns⁻¹)			0.56	≥0.13	0.47	0.30	0.45	0.33		0.37
k_{IC} (ns⁻¹)			0.24	≥0.6	≤0.01	0.24	≤0.01	0.27		0.011
k_{ISC} (ns⁻¹)			0.26	≥9.5	0.20	5	0.17	1.5		0.70
λ_{max}(T−T)			360[b]	385	470	460	530	600		630
ϵ_T (10⁴ M⁻¹ cm⁻¹)		0.21	-	1.1	0.90	1.72	1.2	2.4		3.2

[a] (P) means predicted from a plot of $1/n$ vs E(max). [b] Data in dioxane. [c] Data in benzene. [d] The italicized wavelength is the band maximum. The other one is another distinct band (see Figure 3).

avoiding by this way external interferences. The ϕ_F value was obtained by correcting the compression of the solvent, done by assuming a shrinkage of 20% of ethanol solvent on going from 293 K to 77 K.

All the molar extinction coefficients (ϵ) are a result of more than seven solutions of different concentrations. The slope of the plot of the absorption values (at the maximum wavelength of absorption) vs the concentration values gave us the ϵ values.

Special care was taken to obtain the fluorescence data (ϕ_F and τ_F) and absorption data (ϵ) by running the spectra and lifetimes immediately after the solutions were prepared. This precaution was important for acetonitrile as solvent since chemical degradation of the solutions was observed.

The fluorescence lifetimes, τ_F (mean deviation of three independent measurements, ~5%), were measured by a Spex Fluorolog-τ2 system, which uses the phase modulation technique (excitation wavelength modulated in the 1−300 MHz range; time resolution ~10 ps). The frequency-domain intensity decay (phase angle and modulation vs frequency) were analyzed with the Global Unlimited (rev. 3) global analysis software.[19]

The experimental setup used for determining the triplet spectra and yields was that described elsewhere.[20,21] The excitation wavelength of 355 nm from a Nd:YAG laser (third harmonics) in the nanosecond flash photolysis experiments (pulse width ~7 ns and energy <3 mJ pulse⁻¹). Absorption spectra were constructed based on measurements every 10 nm over the 300−800 nm spectral range, averaging at least 10 shots per wavelength recorded. The triplet lifetimes were measured with laser fluence ≤1 mJ pulse⁻¹. The triplet−triplet molar extinction coefficients (ϵ_T) in acetonitrile were evaluated by use of benzophenone as energy donor (ϵ_T = 6500 M⁻¹ cm⁻¹ at absorption maximum in acetonitrile).[22] Instead, in benzene the triplet yields were determined by energy transfer to β-carotene [23] and by use of benzophenone as reference (ϕ_T = 1).[22] For bifuran the triplet determinations (triplet−triplet spectra and triplet formation quantum yield) were obtained in Applied Photophysics LKS.60 laser flash photolysis spectrometer using a Spectra-Physics Quanta-Ray GCR-130 laser with λ_{exc} = 266 nm and a Hewlett-Packard Infinium oscilloscope.

The product $\epsilon_T \times \phi_T$ for each compound was obtained by the laser energy effect on the change of absorbance (ΔA) measured at λ_{max} for each compound and by use of an optically matched solution ($A_{355} \approx 0.2$) of benzophenone in acetonitrile ($\epsilon_{520} \times \phi_T$ = 6500 M⁻¹ cm⁻¹)[22] to calibrate the instrumental response. Plots of ΔA vs laser dose were linear and passed through zero, thus indicating that only one-photon processes were occurring. In acetonitrile, the triplet yields (experimental error ±15%) were then obtained from the experimental. of ϵ_T

TABLE 2: Photophysical Data for the Oligofurans F2−F4 in Three−Four Different Solvents

Fn	solvent	λ_{max}(abs)	ϕ_F	τ_F/ns	ϕ_T	$\tau_T(\mu s)$	k_F/ns⁻¹	k_{ISC}/ns⁻¹
F2	acetonitrile	282	0.51	0.91		39	0.56	0.27[a]
	ethanol	281	0.53	0.86			0.62	0.28[a]
	dioxane	283	0.63	0.90	0.24	102	0.70	0.27
F3	acetonitrile	329	0.74	1.56	0.31	13	0.47	0.20
	ethanol	329	0.70	1.50			0.47	0.21[b]
	dioxane	331	0.78	1.45			0.54	0.21[b]
	benzene	334	0.77	1.30	0.35	34	0.45	0.27
F4	acetonitrile	361	0.79	1.74	0.29	14	0.45	0.17
	ethanol	360	0.78	1.8			0.43	0.16[b]
	dioxane	364	0.82	1.67			0.49	0.17[b]
	benzene	367	0.80	1.40	0.33	67	0.57	0.24

[a] Assuming the ϕ_T value obtained in dioxane. [b] Assuming the ϕ_T value obtained in acetonitrile.

$\times \phi_T$ and ϵ_T, while in benzene the ϵ_T values were obtained from the experimental $\epsilon_T \times \phi_T$ and ϕ_T.

All measurements were carried out at 22 ± 2 °C; the solutions were saturated by bubbling with argon, unless otherwise indicated.

The lowest excited singlet states, electronic structures, and transition probabilities of polyfurans were calculated by the semiempirical method INDO/1-CI[24] (ZINDO module of Cerius² 3.8 package). The geometries of the substrates were optimized by an ab initio SCF calculation (basis set STO-3G of Gaussian 94).[25] The configuration interaction included only singly excited configurations built from all the occupied molecular orbitals and an equal number of unoccupied MO's.

Results

Table 1 provides data on the (1) longest wavelength absorption band maximum, (2) molar extinction coefficients, (3) fluorescence maximum, (4) quantum yield of fluorescence and triplet occupation, (5) fluorescence lifetime, (6) the rate constants for fluorescence and internal conversion from S_1, as well as that for intersystem crossing, and (7) the $T_1 \rightarrow T_n$ absorption for the oligopolyfurans with n = 2, 3, 4 and some data on n = 1, as well as similar information on the oligopolythiophenes with the same n values (plus n = 5). Table 2 compares absorption maxima, fluorescence and triplet state occupation quantum yields, fluorescence lifetimes, triplet lifetimes, fluorescence rate constants, and intersystem rate constants of F2 to F4 in three to four different solvents. Figures 1−5 show, respectively, for F2−F4 (1) a combination of the absorption and emission spectra in ethanol at 293 and 77 K (2) the absorption spectra alone including furan, where furan has a weak band at ~275 nm (ϵ ~ 30 M⁻¹ cm⁻¹) in addition to the stronger band at ~210 nm (ϵ ~ 7200 M⁻¹ cm⁻¹), (3) emission spectra

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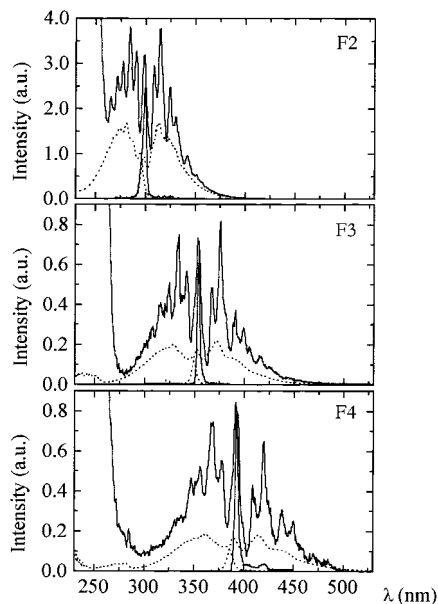*J. Phys. Chem. A, Vol. 104, No. 30, 2000* **6909**

Figure 1. Absorption and emission spectra of the polyfurans in ethanol at 293 K (···) and 77 K (—).
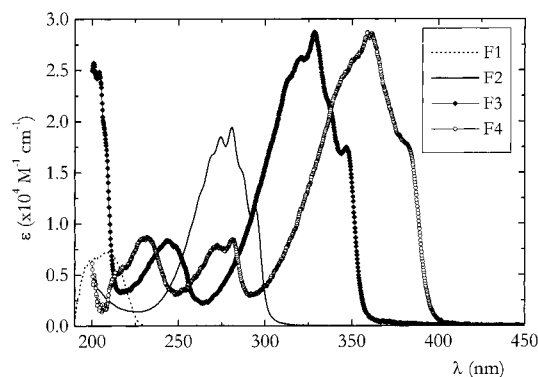

Figure 2. Absorption spectra of furan and polyfurans F1−F4 in acetonitrile at 293 K.
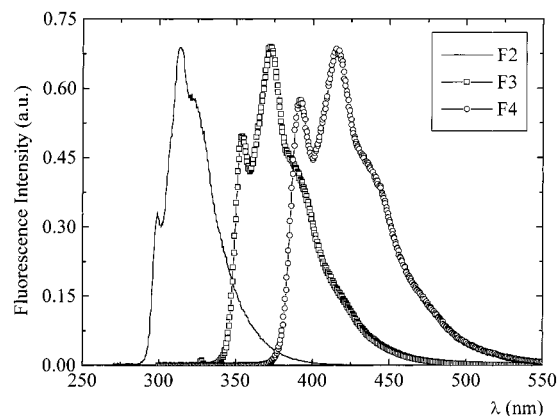

Figure 3. Fluorescence emission spectra of polyfurans F2−F4 in acetonitrile at 293 K.

alone, (4) a plot of $1/n$ (where n is the number of furan rings) vs the absorption maxima and 0−0 band (obtained from the overlap of the absorption and fluorescence spectra), and (5) the triplet−triplet absorption spectra.

The absorption spectra in acetonitrile, ethanol, and dioxane have similar maxima and band shape; see for example data in Table 2.
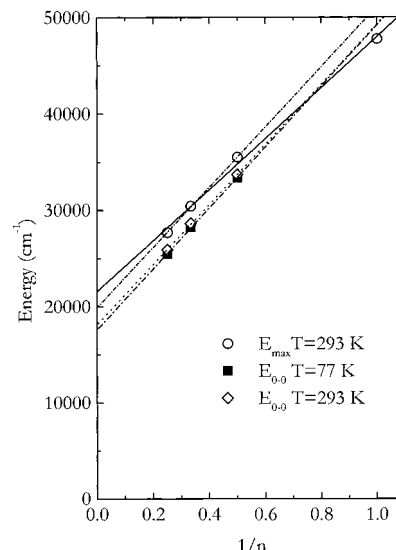

Figure 4. Energy of the 0−0 band for $S_1 \leftarrow S_0$ transition at 293 and 77 K and energy of the absorption maxima for the oligofurans as a function of the reciprocal of n. In case of the absorption maxima data, two linearizations are made: one including F1 (—) and the other excluding F1 (-·-·-).
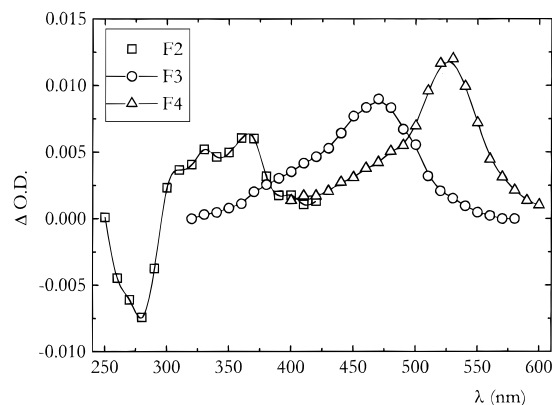

Figure 5. Triplet−triplet absorption spectra of F2 ($\lambda_{exc} = 266$ nm), F3 and F4 ($\lambda_{exc} = 355$ nm) in acetonitrile.

Discussion

Relative to absorption maxima, furan (F1) and the di- (F2), tri- (F3), and quarterfuran (F4) are all blue-shifted from their oligopolythiophene (Tn) analogues (from ∼4300 to ∼2200 cm^{-1}), see Table 1. An interesting observation is that the difference for the dimers (F2 and T2) is ∼2300 cm^{-1} and for the F3−T3 and F4−T4 pairs, the differences are nearly the same ∼2100 cm^{-1}. Plots of $1/n$ vs E_{max}(293 K), E_{0-0}(293 K), and E_{0-0}(77 K) (Figure 4) are all linear. Extrapolation to F5 predicts a value of the maximum to be 382 nm. The difference beween the maxima of the pentamers F5 and T5 is then ∼2000 cm^{-1} which again is comparable to that of all of the other pairs which have the same n (2−4) value (2000−2300 cm^{-1}). The $n = 1$ pair (F1−T1) has a difference of ∼4300 cm^{-1} where this is 2-fold greater than that of the other Fn−Tn pairs. Thus, except for the furan−thiophene comparison, the differences are almost constant. This would indicate a relatively constant difference in the electron delocalization from $n = 2−5$ between the Fn's and the Tn's with greater delocalization existing for the oligopolythiophenes, including thiophene itself.

The difference in energy between the absorption maxima of the various Fn's decreases rapidly from 12 400 cm^{-1} (F1−F2) to 7760 cm^{-1} (F2−F3), 2790 cm^{-1} (F3−F4), and 1520 cm^{-1}

(F4−F5). Interestingly, there is less than a 10% difference is the comparable polythiophene pairs except for T1−T2 which is 10 200 cm^{-1}.

When going to low temperature there is a red shift of the 0−0 band of F2 to F4 ranging from ∼450 to 700 cm^{-1}—a similar result is true for the maximum (if the third band is always considered to be the maximum) (Figure 1). Recall that in the case of the polythiophenes there was a much larger shift (∼1600 cm^{-1}) of the maximum compared to the 0−0 band (∼300 cm^{-1}).[1] Furthermore, there is some better resolution of the absorption at 298K for the polyfurans compared to the polythiophenes and this difference becomes more marked at 77 K (Figure 1). Also note that the shape of the absorption bands of all at 298 K are Franck−Condon (FC) forbidden in character (Figures 1 and 2). However, at 77 K, not only is there a marked increase in vibrational resolution, but there is also a significant redistribution in the vibrational band intensities (Figure 1), whereby the 0−0 band is notably relatively increased in intensity in all cases. In the case of F3, the 0−0 band becomes essentially equal intensity to the one constituting the maximum and for F4, the 0−0 band becomes dominant (Figure 1). All of the foregoing portend an increase in the planarity of the virtual molecule at 77 K compared to 293 K. Thus, the ground and excited state potential energy minima become essentially aligned but, this is not quite true for F2. In the case of F2, it is believed that both trans and cis forms exist at room temperature. In all cases there is less electronic−torsional coupling than for the polythiophenes.

In the case of fluorescence for the polyfurans, there is a smaller but nearly equal red shift (∼200−350 cm^{-1}) of both the 0−0 and maxima bands compared to absorption (450−700 cm^{-1}) when going from 293 to 77 K—the latter is parallel to the results for the polythiophenes. Also there is a greater resolution at 77 K compared with 293 K (Figures 1 and 3), as well as a greater change than for the polythiophenes. Also note that the 0−0 bands of absorption and fluorescence are essentially coincident (Figure 1), which was not quite the case for the polythiophenes. The sum of the foregoing considerations indicates a quite highly planar virtual molecule for the polyfurans at 77 K and quite planar at 293 K (but remember there may be trans and cis forms for F2).

Table 1 presents an absorption and photophysical data comparison of F1−F4 with S1−S4 in acetonitrile. Note from F2 to F4 there is a progressive increase in the fluorescence quantum yield but the change is very small from F3 to F4 (0.74 vs 0.79 and 0.51 for F2). On the other hand, although there is also a progressive increase in the yields for T2 to T4, the actual magnitudes of the yields are very much less than for F2 (50-fold less) to F4 (5-fold less) (Table 1). Also, the change from T3 to T4 is quite significant, 3-fold vs no change for F3 to F4. Similar trends are also seen for the lifetimes of fluorescence, and the difference between F3 and F4 is also very small as for the fluorescence yield whereas there is a 3-fold change for T3−T4 (as there is for the ϕ_F).

Of course, as for the lowest singlet−singlet transition, there is a red shift in the triplet−triplet absorption maximum (assuming there is only one T−T transition) of the polyfurans compared with the polythiophenes.

For the triplet yield, there is essentially no difference among all of the F2−F4 (0.21, 0.28, 0.25) which was not at all true for the corresponding thiophene analogues where there was a real decrease (0.93 to 0.71). The triplet lifetimes of F2 in acetonitrile (32 μs) is considerably longer than for F3 and F4 (13 μs), Table 1.

The sum of ϕ_F and ϕ_T for F3 and F4 is essentially one so that there is insignificant internal conversion from the S_1 state. For F2, there is considerably more internal conversion (∼0.28). For the polythiophenes, the internal conversion is generally only in the 0.05 range except for S4 where it may be 0.13—the T2 has much less internal conversion than does F2 (0.06 vs 0.28).

The magnitudes of k_{ISC} for F2 to F4 are nearly the same (0.17−0.23) and are smaller than k_F by ∼2.5-fold. On the other hand, for the polythiophenes the reverse is true whereby the k_{ISC} are ∼60-fold (T2) to 5-fold (T4) *greater* than the k_F. Also, the k_{ISC} decreases significantly from T2 to T4 (≥ 9.5 to 1.5) rather than staying about constant as for the polyfurans; note how much greater are the k_{ISC} for the polythiophenes compared with the polyfurans even at the smallest value (1.5 for T4 and 0.17 for F4).

In ethanol, for F2−F4 the fluorescence yields and lifetimes are quite similar to acetonitrile (and benzene for F3 and F4). This general pattern of photophysical parameters being quite solvent independent was also seen for the comparable polythiophenes.[1]

With all of the above information, we can reach some further definitive conclusions. The markedly higher energy for the first absorption band of the polyfurans compared with the polythiophenes indicates less π-electron delocalization of oxygen compared with sulfur which is not unexpected. Overall enhancement of this π-delocalization effect with ring addition is greater for the polythiophenes than for the polyfurans up to and including $n = 3$. However, upon going to $n = 4$ and $n = 5$, the differences in the energy of the band maxima are the same for the polyfurans and the polythiophenes indicating that for $n > 3$ there is no net difference in the delocalization energy between the polythiophenes and the polyfurans. This is interesting in that it indicates that, *although delocalization energy continues to increase with ring addition, the incremental change is independent of the nature of the heteroring/atom after $n = 3$*.

The k_F values for F2−F4 are remarkably constant (0.56−0.45) and solvent independent (Table 1). These correspond to intrinsic lifetimes ($\tau°_F$) values of 1.8 to 2.2 ns which are clearly typical of those associated with allowed π,π^* states. Thus the lowest excited singlet state is (1) ^1B_u (or $^1B_1$) in character and *not* ^1A_g.

It is clear that the fluorescence yield is high for F2−F4 and much greater than for T2−T4 (5−40-fold) (Table 1). For F2−F4, the triplet yield is 2−3-fold *less* than the fluorescence yield while for T2−T4, it is 70−4.5-fold *greater* than the fluorescence yield. This is also reflected in the k values where the k_{ISC} values are about 2-fold *less* than the k_F values for F2−F4 while they are 60−5-fold *greater* for T2−T4. It is obvious that the magnitude of the overall spin−orbital coupling is considerably greater for the polythiophenes than for the polyfurans which is not unexpected since the spin−orbital coupling factor for sulfur is clearly greater than for oxygen. However, there is something considerably different regarding how the k_{ISC} changes for the polyfurans compared with the polythiophenes (Tn). In the latter case, there is a large *decrease in k_{ISC} from T2 to T4* (∼6+ fold) whereas k_{ISC} is essentially *constant for the polyfurans*. In our earlier work on the polythiophenes,[1] we discussed the fact that, based on the trend in the k_{ISC}, most of the spin−orbital coupling was not simply due to the classical heavy atom effect[26] but was mediated by charge transfer matrix elements of the type $\langle^1\Psi_{CT}|H_{SO}|^1\Psi_i\rangle$ where the operator contains the spin−orbital coupling factor for sulfur. In the case of the polyfurans, there is "no" decrease (or increase) in k_{ISC} with increasing number

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TABLE 3: Lowest Transition^a Energy (S$_1$ ← S$_0$) and Oscillator Strength, *f*, for the (oligo)Polyfurans (F*n*) Calculated by INDO/1-CI after Geometry Optimization with STO-3G

F*n*	λ/nm (S$_1$ ← S$_0$)	*f*	F*n*	λ/nm (S$_1$ ← S$_0$)	*f*
F1	226	0.21	F4	358	1.08
F2	295	0.62	F5	372	1.35
F3	334	0.80			

^{a} See Table 1 for experimental values.

of rings so we believe in these cases the spin−orbital coupling is primarily due to the classical heavy atom effect (for oxygen) alone.

Adding rings to the polyfuran system and therefore potentially adding more torsional degrees of freedom, as viewed via k_{IC}, apparently does not occur since k_{IC} is essentially negligible in F3 and F4; see Table 1. The k_{IC} is larger in F2 but remember that there may be both trans and cis isomers present at room temperature and we cannot clearly know what the consequences of this is on the net internal conversion.

There is a considerably greater solvent−solute interaction with the polyfurans than with the polythiophenes. This can be rationalized based on expected greater dipole−dipole interaction for the polyfurans compared with the polythiophenes.

There is some disagreement on the nature of the conformers potentially present in solution, see the Introduction. We carried out different types of calculations for F2 and F3 to see if we could clarify some of the issues regarding the type of conformers present or whether twisting occurred around the inter-ring C−C bond to any significant extent.

Calculations of the lowest singlet transition of the trans configuration using STO-3G optimization gave the results in Table 3. For F2 and F3, angles of twist up to 30° resulted in a 2−3 nm shift. Comparison of the F2 cis and trans conformers where optimization was by PM3, also gave shifts of 2−3 nm. These results indicate a shallow ground state potential energy curve as was also found for the polythiophenes.[1] Other calculations that we did began with the planar conformer, and transition energies were calculated as a function of angle of twisting using ZINDO/S-CI. For F2, twisting by 20° and 30° gave shifts (blue) of 3 and 7 nm respectively. These changes did bring the energies into close harmony with experiment. All of the above indicate that any twisting is likely confined to 20°−30° and that the cis conformer is quite similar to that of the trans regarding the lowest transition energy.

Further, AM1 calculations of F2 predict that the cis is 0.09 kcal/mol more stable than the trans. For F3 and F4, similar type of calculations indicate the cis to be more stable than the trans but only by ≈0.1−0.2 kcal/mol. Given the reliability of such calculations, it is not possible to unequivocally believe the results. It is clear that the energy difference of the cis and trans conformers of F2 is small and that conformer equilibrium in solution at room temperature is possible.

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