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Leandro A. Estrada


Victor A. Montes

Grigory Zyryanov

Pavel Anzenbacher Jr.

Bowling Green State University, pavel@bgsu.edu

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Triplet Energy Studies of Thiophene and *para*-Phenylene Based Oligomers

Leandro A. Estrada, Victor A. Montes, Grigory Zyryanov, and Pavel Anzenbacher, Jr.*

Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403

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A series of conjugated materials based on oligomers of the *para*-phenylene type and oligothiophenes was prepared, and their phosphorescence spectra were recorded at 77 K using a pulsed flash-lamp as a light source and gated detection. The triplet energies of the oligomers were estimated and correlated with their chemical structure. It was found that simple changes in the building block sequence in the thiophene-containing oligomers allowed for tuning the triplet energy from 1.86 to 2.35 eV (530–670 nm). Hypsochromic shifts and little variation of the triplet energy were obtained with increasing length of the π -system for thiophene end-capped oligomers, contrary to the usual behavior of unsubstituted oligomers. The experimental results were supported with theoretical computations from density functional theory (B3LYP/6-31G*) calculations, which indicated that changes in the geometry and delocalization of the triplet excited state account for the trends in the triplet energy evolution.

Introduction

Conjugated organic oligomers and polymers have received a significant amount of interest because of their use in optoelectronic applications^{1,2} such as organic light-emitting diodes (OLEDs),³ organic photovoltaics (OPVs),⁴ organic field-effect transistors (OFETs),⁵ nonlinear optics,⁶ and organic lasers.⁷ A thorough understanding of their photophysical properties is fundamental to the functioning in many applications where the dynamics of the generated excited states directly influence the device performance resulting from the formation of charge carriers, energy migration, and trapping.^{8,9}

Unfortunately, the triplet excited state energies of many conjugated materials have eluded direct measurement due to difficulties with measuring their low-intensity phosphorescence.⁹ As a result, the triplet energies of archetypal systems such as oligothiophenes and oligomers of the *para*-phenylene type had not been reported until recently,^{9–11} and very few studies report the triplet state energies of their copolymers.¹² Direct measurements of triplet energies are important for correct utilization of conjugated polymers in energy transfer processes, for example, as host materials for triplet-emitting dopants in phosphorescent OLEDs (PHOLEDs)¹³ or for sensitization of singlet oxygen formation.¹² In OLEDs, precise alignment of triplet energy levels is essential for effective triplet energy transfer and for maximizing the performance of doped¹⁴ as well as undoped¹⁵ devices. We have also recently demonstrated that alignment of the triplet energies in donor–bridge–acceptor (DBA) systems can result in improvements of the electroluminescence efficiency by promoting triplet energy transfer in a molecular photonic wire fashion.¹⁶ Therefore, engineering and controlling the triplet energies of conjugated oligomers and polymers is of practical advantage for the construction of efficient optoelectronic devices, namely, PHOLEDs.^{17,14a}

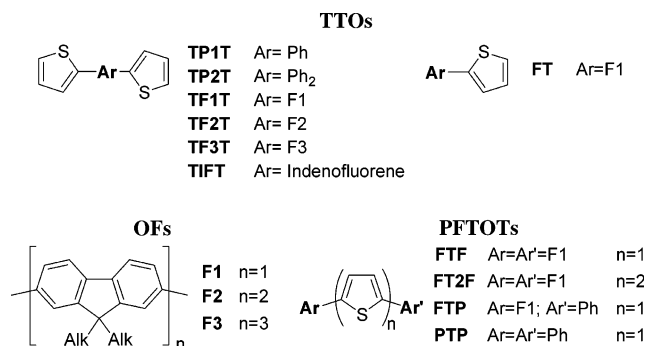


Figure 1. Structures of the synthesized oligomers.

Compared to tuning their singlet excited state energies, both the measurements and tuning of the triplet energies in organic materials is significantly more difficult.^{17,18} To support potential application of conjugated oligomers in PHOLEDs, we decided to investigate the triplet levels of oligomers with triplet energies in the range 1.90–2.30 eV (530–660 nm), which correspond to triplet levels of most dopants. The structurally well-defined oligomers based on thiophene and *para*-phenylene type oligomers presented here allow correlating their triplet energy levels with respect to their structure (Figure 1). Their components were chosen due to their established performance in thin film semiconductor devices,¹⁹ ease of processability, well studied fluorescence,²⁰ and potential use as electronic bridges in molecular wires,^{21,22} as host molecules for red-,²³ infrared-,²⁴ or white-emitting²⁵ electrophosphorescent devices, or as electronic bridges that could be used in self-assembled organometallic electroluminescent materials.¹⁶ The studied oligomers were divided into three groups, oligofluorenes (OFs), thiophene-terminated oligomers (TTOTs), and phenyl-, fluorenyl-terminated oligothiophenes (PFTOTs) (Figure 1). The preparation of these compounds involved short synthetic pathways outlined in the

* To whom correspondence should be addressed. E-mail: pavel@bgsu.edu.

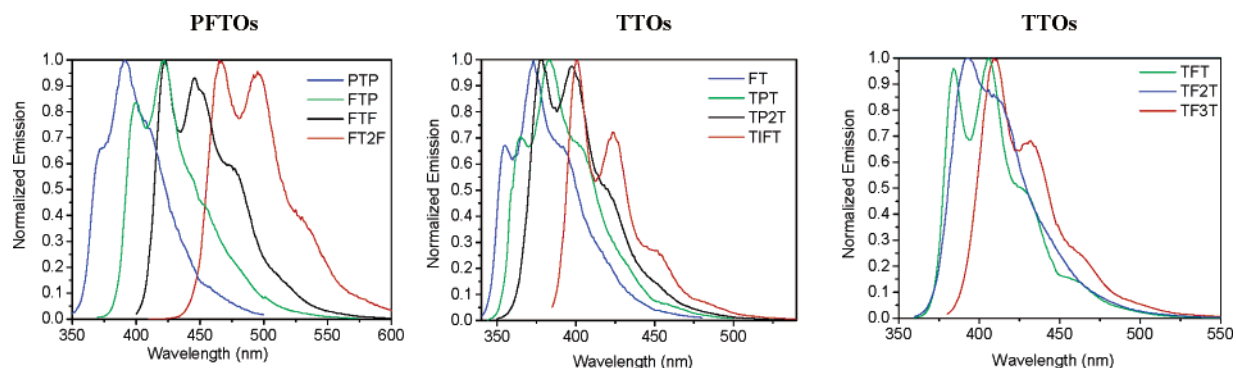


Figure 2. Emission spectra of the prepared oligomers in CH_2Cl_2 at 298 K.

TABLE 1: Spectroscopic Parameters of the Oligomers in Chloroform at 298 K

compound	$\lambda_{\text{abs-max}}$ (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	$\lambda_{\text{F-max}}$ (nm)	Φ_{F}	τ_{F} (ps)	k_{rad} ($\times 10^8 \text{ s}^{-1}$)	k_{nrad} ($\times 10^8 \text{ s}^{-1}$)
FTP	352	42600	422	0.41	510	20	28
FTF	373	54800	423	0.61	650	15	9.7
FT2F	403	58600	465	0.23	470	21	72
FT	328	27500	373	0.35	510	20	36
TPT	324	27500	383	0.50	760	13	13
TP2T	330	42400	378	0.75	839	12	4.0
TFT	352	50900	406	0.97	1010	9.9	0.35
TF2T	351	87100	394	0.71	539	19	7.6
TF3T	369	160000	410	0.66	583	17	8.8
T1FT	371	86900	401	0.82	828	12	2.7

Supporting Information. In general, Suzuki–Miyaura²⁶ and Stille²⁷ cross-couplings afforded the final compounds after bromination via electrophilic aromatic substitution,^{28a} dialkylation of the sp^3 carbons of fluorene and indenofluorene,^{28b} lithium–halogen exchange and borylation reactions.^{28c,d}

Experimental Section

Materials. The preparation of the oligomers was described previously,^{28b,29} except for **FTP**, **T1FT**, **TF2T**, and **TF3T**. Synthesis of indenofluorene was achieved by using a modified Ebel method.³⁰ All compounds were characterized by ^1H NMR, ^{13}C NMR, and mass spectrometry. Our characterization data were in good agreement with the reported data for similar or identical materials.^{28b,29} The complete synthetic procedures and characterization for the studied compounds are listed in the Supporting Information.

Spectral Measurements. Absorption spectra were recorded using a Hitachi U-3010 double-beam spectrophotometer, accurate to ± 0.3 nm. For UV–visible measurements, the concentration of the solutions was $1.0 \mu\text{M}$ in spectroscopic grade CH_2Cl_2 . The Beer law was confirmed for solutions with concentrations between 1 and $10 \mu\text{M}$ and employed for calculations of the molar decadic absorption coefficient (ϵ).

Steady state, time-resolved fluorescence, and phosphorescence measurements were performed on a single-photon-counting spectrofluorimeter from Edinburgh Analytical Instruments (FLSP 920) equipped with a pulsed Xenon flash-lamp ($\mu\text{F}920\text{H}$, 200–900 nm, 10–100 Hz) for time-gated experiments. For fluorescence measurements, solutions with optical densities below 0.1 at the wavelength of excitation were prepared in spectroscopic grade CH_2Cl_2 .

For phosphorescence studies at 77 K, the compounds were dissolved in solvent mixtures of spectroscopic grade 2-methyl-tetrahydrofuran (MeTHF), methanol/ethanol (1:1), and ethyl iodide (EtI, 10% v/v) with optical densities ranging between 0.1 and 0.3. The ethyl iodide component was introduced to partially enhance the typical weak phosphorescence of organic compounds. To avoid residual fluorescence in the measurement

of the phosphorescence spectra, the signal acquisition of the photomultiplier tube (PMT) was electronically gated. Typically, delay times longer than $5 \mu\text{s}$ and gate widths of 25–2000 μs were used. Oligofluorenes **F1–F3** and compound **PTP** were used to compare the results obtained using our setup with reports employing laser excitation. Their phosphorescence spectra showed excellent agreement with the published data (see the Supporting Information).^{9–11a}

Results and Discussion

The fluorescence spectra of all oligomers are shown in Figure 2, and the corresponding photophysical data recorded at room temperature are summarized in Table 1. In general, higher absorption coefficient (ϵ) values as well as lower energies for the $\text{S}_1 \rightarrow \text{S}_0$ transition were determined for systems with a higher number of conjugated bonds and corresponding extension of the π -system. Interestingly, oligomers of the TTO series exhibited higher emission energies and higher fluorescence quantum yields than those of the PFTO series, despite the higher content of thiophene units in the TTOs. We presume that the singlet excited state density in TTOs is localized on the central arylene moieties with only a minor amount of the singlet excited state density residing on the thiophene units of TTOs, as sulfur atoms would lower the efficiency of radiative processes from S_1 by promoting intersystem crossing.¹² The effect of localized triplet excited states in TTOs was also investigated and is discussed (vide infra).

The phosphorescence spectra of the oligomers at 77 K (Figure 3) were measured using a gated-detection technique. In general, lifetimes in the millisecond regime were recorded for the phosphorescence decay, which is in agreement with the long-lived nature of triplet excited states (see the Supporting Information).³¹ Also, the vibrational progression observed in the phosphorescence spectra coincides with the vibrational pattern observed in the corresponding fluorescence spectra.

Depending on the structure of the oligomers, the determined triplet energies ranged from 1.86 to 2.35 eV. The position of the thiophene ring within the oligomer played a central role in

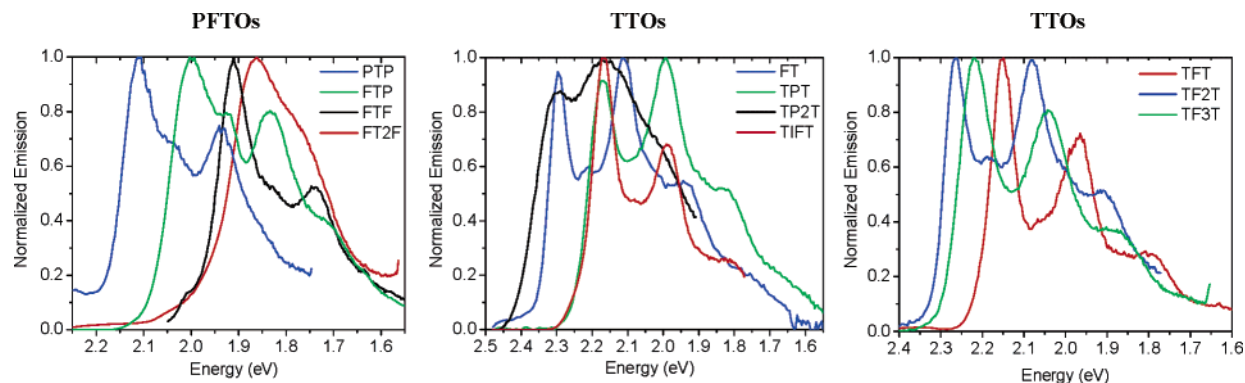


Figure 3. Phosphorescence spectra of the oligomers at 77 K.

TABLE 2: Photophysical Properties of the Oligomers at 77 K

molecule	$S_1 \leftarrow S_0$ (eV)	$S_1 \rightarrow S_0$ (eV)	$T_1 \rightarrow S_0$ (eV)	ΔE_{S-T} (eV)
FTP	3.52	2.94	1.99	0.95
FTF	3.32	2.93	1.91	1.02
FT2F	3.07	2.67	1.86	0.81
FT	3.78	3.47	2.29	1.18
TPT	3.83	3.24	2.18	1.06
TP2T	3.76	3.28	2.29	0.99
TFT	3.52	3.23	2.15	1.08
TF2T	3.53	3.15	2.35	0.80
TF3T	3.36	3.02	2.26	0.76
TIFT	3.34	3.09	2.16	0.93

the phosphorescence and triplet energy of these molecules. Oligomers with internal thiophenes (PFTOs), in which the thiophene has aryl substituents in positions 2 and 5, exhibited the lowest triplet energies (1.86–2.00 eV). Their triplet energies were found to decrease with an increasing number of thiophene moieties and with a higher number of double bonds in the π -conjugated system (Table 2). In contradistinction, the phosphorescence spectra of monosubstituted thiophenes (TTOs) afforded higher triplet energy values (2.15–2.35 eV) even in the case of large conjugated oligomers. Even more interesting was the evolution of the triplet energy in the TTO series, which showed an unusual trend with increasing length of the oligomer. Hypsochromic shifts were obtained for **TP2T**, **TF2T**, and **TF3T** compared to the shorter **TPT**, **TFT**, and **TIFT** oligomers, which displayed an almost constant triplet energy around 2.16 eV (Table 2). The exchange energies of all of the oligomers range between 0.76 and 1.18 eV, which is in agreement with the previous studies of polymer systems based on similar structural units ($\Delta E_{S-T} = 0.7\text{--}0.8$ eV).³²

The intriguing behavior of the triplet excited state in TTO series was rationalized by density functional theory (DFT) calculations. For the short oligomers **TPT**, **TFT**, and **TIFT**, a fully planar geometry is favored for the triplet state. This planarization results in delocalization of the excitation over the entire molecule and low-energy minimum. For longer oligomers,

TABLE 3: Theoretical and Experimental Triplet Energy Values for Thiophene-Containing Oligomers

oligomer	calculated E_T (eV)	experimental E_T (eV)
PTP	2.08	2.10
FTP	2.00	1.99
FTF	1.92	1.91
FT2F	1.63	1.86
FT	2.31	2.29
TPT	2.17	2.18
TP2T	2.27	2.29
TFT	2.24	2.15
TF2T	2.37	2.35
TF3T	2.27	2.26
TIFT	2.27	2.16

however, the optimized geometry of the triplet excited state deviates from planarity. This electronic decoupling results in delocalizing the excitation over fewer atoms and results in higher triplet energies (Figure 4).

The triplet energies of all oligomers were also estimated by DFT calculations using the method proposed by Beljonne et al.¹⁰ and compared with results from the phosphorescence measurements. The experimental trends in PFTOs and TTOs were satisfactorily reproduced by the computations (Table 3). Also, the experimental values agreed with the calculated ones with a systematic underestimation of ~ 0.13 eV, most likely due to the fact that the calculations were carried out for the oligomers in vacuum. In the near future, this approach is expected to yield a bridge with a triplet energy of 2.00 eV to promote triplet energy transfer from aluminum tris-8-quinolinolate (${}^3\text{Alq}_3 = 2.17 \pm 0.10$ eV)³³ to platinum(II) tetraphenylporphyrin (${}^3\text{PtTTP} = 1.91$ eV)³⁴ via the incoherent hopping mechanism.^{16,22b} The DFT calculation predicted that a mixed oligomer comprising a thiophene unit substituted with fluorene and a phenyl group was necessary to achieve the target triplet energy of 2.0 eV. Indeed, **FTP** displays phosphorescence with the first vibronic band at exactly 1.99 eV in accord with the calculation (Figure 3). Efforts toward the preparation of an electroluminescent triad that includes this electronic bridge are currently underway.

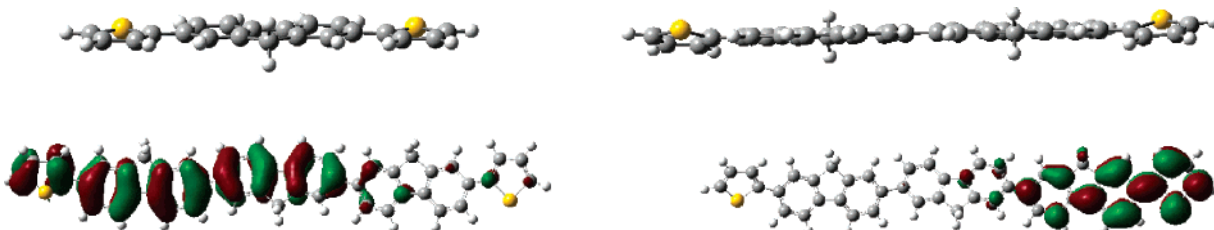


Figure 4. (top) Optimized geometries for the triplet excited states of **TFT** and **TF2T** showing the differences in planarity. (bottom) Single-occupied molecular orbital (SOMO) densities of **TF3T** indicating different distributions of alpha and beta spins over the molecule.

These data show that the simple rearrangement of the building blocks in the oligomers allow for tuning of their triplet energy. The series of thiophene-terminated oligomers (TTOs) displays hypsochromic shifts in the triplet energy evolution due to confinement of the triplet wavefunction as confirmed by recording their phosphorescence spectra and by quantum chemical calculations at the DFT level.

Conclusions

A series of oligomers utilizing fluorene, indenofluorene, thiophene, and phenyl building blocks in varying sequence was prepared to gain insights into the structural correlation of the triplet excited state energies. It was shown that the extension of the π -system as well as the substitution pattern of thiophene governs the emission properties in the studied oligomers. Fluorene–thiophene–phenylene (FTP) with a triplet energy of 1.99 eV was found to be a promising candidate for use as an electronic bridge in Alq₃–bridge–PtTPP triads that display molecular photonic wire behavior.¹⁶ Phosphorescence spectra recorded at 77 K exhibited lifetimes in the millisecond regime and vibrational progressions consistent with the vibrational modes of the fluorescence spectra. Interestingly, the sequence of the building blocks within the oligomers significantly effects the delocalization and energy levels of triplet excited states, while the effect on singlet excited states appears to be minimal. The experimental triplet energies of the studied materials agreed satisfactorily with the theoretical values estimated from DFT studies (B3LYP/6-31G*).

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Supporting Information Available: Synthetic procedures and characterization of all compounds, experimental details of the measurements, and DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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