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Dynamic Broadening Alters Triplet Extinction Coefficients in Fluorene Oligomers and Polymers

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ABSTRACT

We report $T_n \leftarrow T_1$ spectra and extinction coefficients, ϵ , and other properties as functions of chain length for a series of fluorene oligomers, oF_n , and polymers, pF_n , with $n = 2$ -84 repeat units. We find ϵ increases with length, peaking at $159,400 \text{ M}^{-1}\text{cm}^{-1}$ for oF_3 , and then decreases for longer chains. ϵ does not scale with $1/n$ or e^{-n} to reach a constant value at long length, as predicted by the commonly applied oligomer extrapolation approximation, although spectral shifts, oscillator strengths and transition dipole moments do reach limiting values for chains near 10 units long. While computations describe the triplet in oF_2 and oF_3 as having similar geometries with a single flattened dihedral angle between units, computations and simulations suggest that in longer oligomers motion along the chains of the short 2-3 unit long T_1 state is probably the source of the unusual changes in ϵ . These occur because hopping along the chain is sufficiently fast that the dihedrals between fluorene units can not fully relax. At a length near 10 units, hopping and dihedral angle changes produce a steady state distribution of geometries with only small changes from the ground state, which persist for longer chains. Additional decreases in ϵ from pF_{28} - pF_{84} are plausibly due to a small number of chain defects which result in loss of triplets.

I. INTRODUCTION

Conjugated polymers are key components in “plastic electronics” due to their ability to act as both conductors for charges and excitons and their ability to absorb or emit photons. Understanding of these properties is key for improving the design of conjugated polymers used in applications such as organic photovoltaics (OPV),¹⁻³ organic light emitting diodes (OLEDs),⁴⁻¹² and molecular electronics.¹³ Derivatives of polyfluorenes have been applied in these areas, as

well as other novel opto-electronic applications.¹⁴⁻¹⁷ Excitons and excess charges on these materials are known to be delocalized over a number of repeat units as polarons, depending on the nature of the polymer.¹⁸⁻²² The importance of delocalization has led several groups to examine how oligomer length affects the properties of charges and excitons in solution.²³⁻³⁰ A particular interest in triplet excitons stems from their potential to support alternative visions of triplet-based OPV utilizing long distance triplet transport.^{9, 31}

A valuable aid to understanding has been the oligomer extrapolation approximation,^{27, 32} which notes that many properties, for example excited state absorption spectra, fluorescence and phosphorescence spectra, shift consistently with oligomer length until they approach an effective conjugation length or delocalization length of the polaron.³³ Beyond this length many properties become constant, taking on values characteristic of the corresponding polydisperse polymers. This dependence is widely fit in terms of models having roots in a particle in a 1D box,³⁴ using a functional form of $1/n$ or e^{-n} . A modification to such universal scaling was recently proposed by Chen,³⁵ who showed that properties such as triplet free energies and redox potentials have a component due to entropic effects, which results in continued shifts past the delocalization length producing substantial differences between oligomers and polymers.

Triplet excited states of conjugated polymers are of particular current interest because they can efficiently carry excitation energy over long distances on conjugated chains within their lifetime.³⁶⁻⁴⁰ By contrast, singlets typically have exciton diffusion lengths less than 10 nm,⁴¹⁻⁴⁷ though recent work established that they can be as much as 34 nm in solution.⁴⁸ Triplets in conjugated polymer have been shown to be more localized than singlets in both liquid^{27, 49-52} and solid phases.^{29, 53} Their motion along and between chains is governed by electronic coupling through the Dexter exchange mechanism. The short range of Dexter couplings might be expected

to make triplet motion very sensitive to polymer structure and to defects. Wasserberg examined length-dependence of $T_n \leftarrow T_1$ absorption spectra of oligo and polyfluorenes in low temperature glasses,²⁹ but there are no reports of the corresponding extinction coefficients, necessary for quantitative probes of dynamics and transport of triplets. Triplet formation is an energy loss mechanism in OPV and OLEDs, and extinction coefficients are needed to know how many are formed. In solution, excitation of conjugated polymers in the presence of electron donors (D) or acceptors (A) or with D or A attached yields rich photophysics including ET reactions that may produce triplets.^{40, 52} In polymer films triplet formation often has a central role. Quantitative interpretation of all these experiments requires knowledge of the extinction coefficients of the triplets. Indeed, knowledge of triplet extinction coefficients might often be key to understanding such experiments. While spectra of many triplets have been examined, extinction coefficients are less available. For many conjugated polymers low intersystem crossing yields make measurements of extinction coefficients of triplets difficult. This work reports room temperature measurements in solution of triplet extinction coefficients, triplet transfer rates and $T_n \leftarrow T_1$ spectra for 9,9-dihexyl-fluorene oligomers (oF_n) and polymers (pF_n) with lengths of n = 2 to 84 repeat units. The method used is pulse radiolysis, which can produce triplets quickly and in large yield without the need for singlet precursors.⁵⁴

During these measurements we found that extinction have an unusual dependence on oligomer length and that spectral widths provide information on the motion of triplets on chains. The results also seek to understand a puzzle. Computation finds triplets to have short delocalization length in part because their optimized geometries have one flat (~ 0 degree) dihedral angle. Movement of a triplet exciton would thus require movement of this substantial

deformation which should be difficult, so transport might be slow. Triplet transport appears to be fast however. The results below will provide understanding of this puzzle.

II. EXPERIMENTAL DETAILS

Chemicals: Synthesis and characterization of oligomeric and polymeric 2,7-(9,9-dihexylfluorenes) followed established methods^{28, 55, 56} and were described previously.^{20, 57} Oligomer samples were synthesized stepwise to have chains with identical length without fractional separation for length, denoted as oF_n, where n is the length in fluorene repeat units. Longer polymers, which are polydisperse, were separated into narrowed length distribution fractions with different average lengths, n, by preparative scale GPC, similarly denoted as pF_n. Average lengths of each fraction were determined by multi-angle light scattering (MALS) using the oligomers as molecular weight standards. Polydispersities of pF_n fractions ranged from 1.5-1.9. Samples were prepared in an inert argon atmosphere glovebox in 0.5 cm path length sealed Suprasil spectrophotometric cells. Solvents used were benzene, toluene or *p*-xylene from Aldrich, dried over 3A molecular sieves. Benzophenone (Aldrich) was sublimed. Steady-state absorption spectra of oF_n have been previously reported in tetrahydrofuran,²² and are given along with those for pF_n in toluene at 21 and -78 °C in the Supplementary Material, Figure S0.

Pulse Radiolysis: Polymer triplets were produced using pulse radiolysis at Brookhaven National Laboratory's Laser-Electron Accelerator Facility (LEAF).⁵⁸ The experiments used < 50 ps pulses of ~9 MeV electrons giving an absorbed dose of about 25 (± 30%) Gy in 0.5 cm cells, producing 3-4 μM solute triplets. Probe light from a pulsed xenon arc lamp, with wavelengths selected by 10 nm bandpass interference filters with 10 nm increments between filters, was detected with a

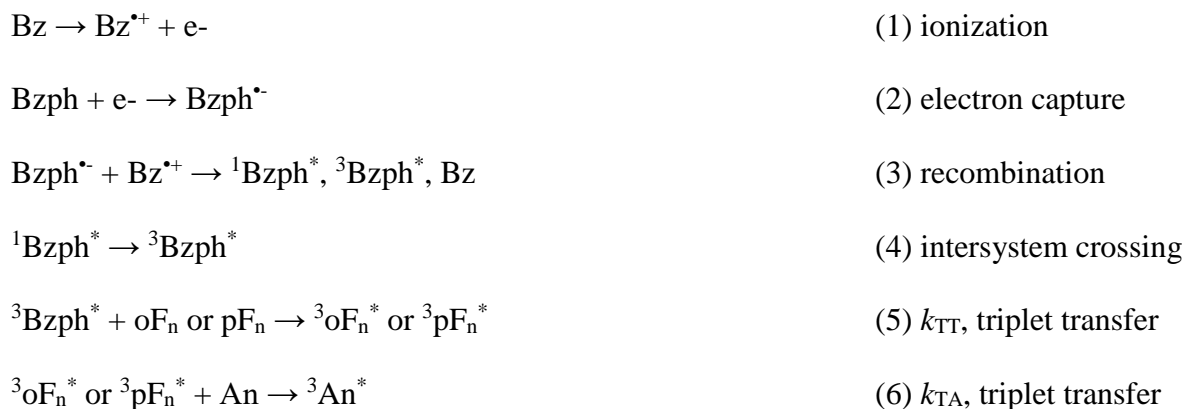
silicon EG&G FND-100Q detector and digitized with either a LeCroy Waverunner HRO 640ZI or HRO 66Zi oscilloscope, giving approximately 1 ns time resolution. Data analysis used the Igor Pro program, with task specific fitting functions.

Computations: Electronic structure computations used the Gaussian09 and Gaussview5 programs.^{59, 60} All geometries were determined using density functional theory (DFT) with the B3LYP functional and 6-31(d) basis set. Triplet excited state transitions were modeled using time-dependent DFT (TD-DFT). No solvation models were used.

III. RESULTS

Production of triplets by pulse radiolysis. Pulse radiolysis can efficiently produce triplet excited states, even for molecules with low triplet quantum yields, and is widely used to

Scheme 1: Primary mechanism for production of polymer or anthracene (An) triplets by pulse radiolysis in benzene (Bz), containing 100 mM benzophenone (Bzph).



determine their extinction coefficients.^{54, 61} The current experiments produced 3-4 μ M concentrations of ${}^3oF_n^*$ or ${}^3pF_n^*$ by transfer from a high concentration solute, as shown in Scheme 1. Ionization (1) of solvent molecules was followed by rapid capture (2) of electrons

primarily by 100 mM benzophenone (Bzph). Recombination (3) of $\text{Bzph}^{\bullet-}$ with $\text{Bz}^{\bullet+}$ resulted in production of Bzph^* . About half of these ion-recombination events are expected to form triplets.⁶² The other half form Bzph singlets, $^1\text{Bzph}^*$, which intersystem cross to triplets (4) in 30 ps with unit quantum yield.⁵⁴ The large benzophenone concentration prevents most recombination of e^- with $\text{Bz}^{\bullet+}$, which produces short-lived singlet and triplet Bz^* , but any Bz^* made by recombination or direct excitation will also transfer rapidly to make Bzph^* . Bimolecular energy transfer, equation (5), forms triplets of oligo- or polyfluorenes. The concentrations of oF_n and pF_n used were kept low so that most electrons were captured by Bzph, but high enough that capture of more than 1 triplet per molecule is unlikely, avoiding significant intrachain triplet-triplet annihilation.^{38, 39} In the longest chains, less than 1% may attach more than 1 triplet; for others the fraction becomes vanishingly small. Initial experiments were performed in toluene or *p*-xylene. Triplets of benzophenone were found to have shortened lifetimes due to abstraction of H atoms from these solvent molecules, so benzene was a better alternative when low concentrations of oligomers or polymers were used. Similar results were obtained in any of the three solvents if corrections were applied for the lower yields of triplets transferred to oF' s and pF' s in toluene and *p*-xylene.

Figure 1 shows typical pulse radiolysis data. Each trace is an average of 4 accelerator shots, with per shot correction for electron pulse size fluctuations using a faraday cup after the sample. The concentration of $^3\text{Bzph}^*$ produced was determined at its peak absorbance in benzene at 530nm, using the widely accepted value of $\epsilon(530\text{nm, benzene}) = 7220 \text{ M}^{-1} \text{ cm}^{-1}$.⁶³ oF_n and pF_n were measured in benzene for direct comparison with $^3\text{Bzph}^*$, and to avoid losses due to H atom abstraction. Older reported values of $\epsilon(^3\text{Bzph}^*)$ in benzene were generally larger,^{61, 64, 65} and would result in lower $^3\text{oF}_n^*$ or $^3\text{pF}_n^*$ determinations. The data were fit to yield the oF_n or pF_n

extinction coefficient, and rate of triplet transfer from $^3\text{Bzph}^*$ to the solute. Additional details of the fits are given in Section S1 of the Supplementary Material (SM).

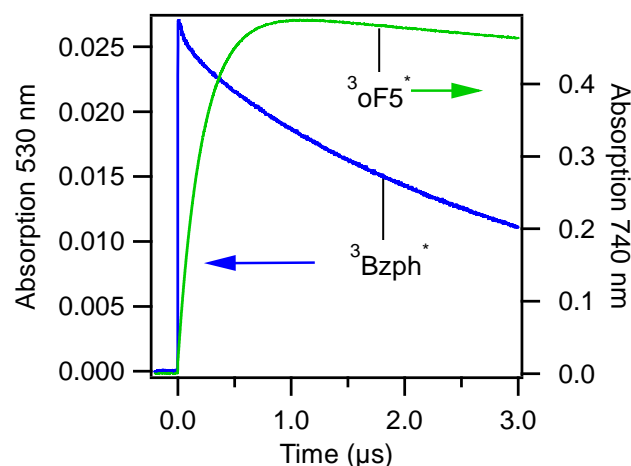


Figure 1. Production of $^3\text{oF}_5^*$ in benzene after by pulse radiolysis. A sample of 100 mM benzophenone (blue, left axis) alone is compared to one with 100 mM benzophenone and 0.6 mM oF₅ (green, right axis).

Triplet-triplet absorption spectra. Figure 2 shows $T_n \leftarrow T_1$ absorption spectra in toluene for oF₁₀ and pF₂₈ along with those previously reported for oF₂-oF₆.³⁵ Spectra for pF₅₇ and pF₈₄ are identical in shape and position to that for pF₂₈ but have lower extinction coefficient, and are not shown. All spectra are assumed to be identical in different aromatic solvents, confirmed with oF₁₀ in benzene, toluene, and *p*-xylene. Each spectrum is scaled here to match the peak extinction coefficients determined in benzene below. The spectra were recorded following pulse radiolysis in toluene at 293 K by a similar method to that in scheme 1, using 30 mM acetophenone instead of benzophenone, and added 10 mM biphenyl or naphthalene to rapidly make an intermediate long-lived aromatic triplet, which subsequently transferred to the oligo and polyfluorenes with high yield. The spectra show a large red shift from oF₂ to pF₂₈, accompanied by noticeable broadening of the bands to oF₁₀, but a slight narrowing for pF₂₈. Wasserberg et

al.²⁹ reported a similar trend for oF₃, oF₅ and pF in 80 K methyl-THF glass, though the 80 K spectra peak at slightly longer wavelengths. The spectrum for pF₂₈ is consistent with previous reports for polyfluorene.^{37, 66} Longer polyfluorenes showed no significant additional red-shift or changes in width. Note that ³oF₂^{*}, peaking at 541 nm, is also red shifted compared ³fluorene^{*}, which has been reported to peak at 376 nm in hexane.⁶⁷ Additional analysis of the spectral shift with polymer length is given in section S2 (SM).

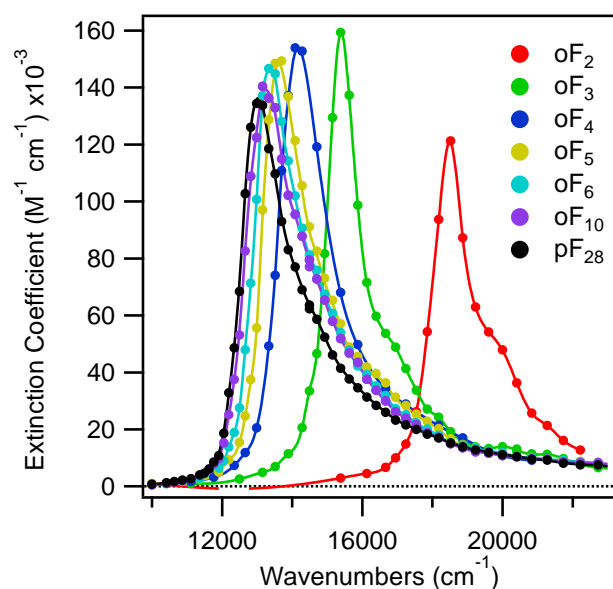


Figure 2. Triplet-triplet absorption spectra of oF₂-oF₁₀ and pF₂₈ recorded in toluene, scaled to the extinction coefficients determined in benzene.

Oscillator strengths, f_n , and transition dipole moments, μ_n , for the $T_n \leftarrow T_1$ transition were determined from the absorption spectra in Figure 2. The oscillator strength gives a measure of the total transition probability, integrated over the absorption band in wavenumbers, $\tilde{\nu}$, determined using Equation 2:⁶⁸

$$f_n = \frac{2.303m_e c^2}{\pi n_0 N e^2} \int \epsilon(\tilde{\nu}) d\tilde{\nu} \quad (2)$$

where n_0 is the sample index of refraction. Kedenburg,⁶⁹ determined n_0 in toluene to be 1.501-1.487 at the peak wavelength of each spectrum. The magnitude of the transition dipole moment between the T_1 and T_n states is related to f_n by equation 3:⁶⁸

$$|\langle \mu_n \rangle|^2 = \frac{3he^2}{8\pi^2 m_e \tilde{\nu}} f_n \quad (3)$$

Figure 3 plots f_n and μ_n as functions of chain length, n . Results for pF₅₇ and pF₈₄ are not included to highlight changes in the oligomers. These long polymers have smaller f and μ due only to differences in extinction coefficient from pF₂₈ as they have identical spectra, and are suggested in the discussion to be due to chain defects. For the oligomers, both f_n and μ_n grow rapidly with n from oF₂ and approach a maximum value for oligomers at 10 repeat units long, saturating at a similar length as the $T_n \leftarrow T_1$ absorption spectral shift. Strong absorption by ground-state polymer prevented measurement for wavelengths less than ~400 nm truncating the triplet spectra on the high energy side. Neglecting any new peaks at wavelengths < 400 nm, this truncation decreases the oscillator strengths by 10% at most. The truncation will affect results for the shortest oligomers, oF₂ the most, however the trends seen in Figure 3 would not be strongly perturbed. The values for pF₂₈ appear to be 3-8% lower than that for oF₁₀. This decrease may be explainable by chain defects, as explored in the discussion section. The magnitudes of the transition dipole moments rival those for $S_1 \leftarrow S_0$ absorptions,^{26, 30} and are known to be oriented along the polymer chain.⁴⁹

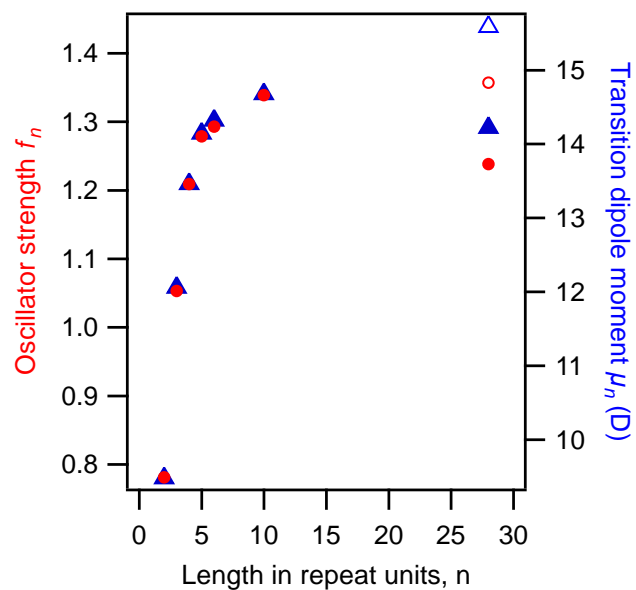


Figure 3. Oscillator strength, f_n , (solid red circles) and magnitude of the transition dipole moment, μ_n (Debye, solid blue triangles), as functions of the number of repeat units in the polyfluorene chain. The open markers for pF₂₈ are corrected for defects, described in the discussion.

Table 1. $T_n \leftarrow T_1$ spectral properties determined by pulse radiolysis in benzene.

Sample	[S] (mM) ^a	Peak λ (nm)	k_{TT} ($\times 10^9$ M ⁻¹ s ⁻¹) ^b	ϵ (M ⁻¹ cm ⁻¹) ^d
<i>p</i> -terphenyl	1.00	460	8.77 ± 0.03	78300 ± 1200
tetrathiophene	3.00	570	6.06 ± 0.08	50100 ± 3700
fluorene (oF ₁)		376		40000 ^c
oF ₂	1.50	541	4.07 ± 0.1	121200 ± 6600
oF ₃	1.00	649	3.87 ± 0.03	159400 ± 5800
oF ₄	0.26	705		153900 ± 6000^e
oF ₅	0.60	735	7.09 ± 0.06	148500 ± 6100
oF ₆	0.56	746		146700 ± 6000^e
oF ₁₀	0.30	757	9.20 ± 0.06	139300 ± 5100
pF ₂₈	0.11	768	23.4 ± 0.2	135200 ± 1700
pF ₂₈	0.21	768	20.8 ± 0.2	137300 ± 4600
pF ₅₇	0.11	770	51.5 ± 0.8	114000 ± 2900
pF ₈₄	0.036	770	72.5 ± 2.6	92000 ± 7300

^aFluorene oligomer and polymer concentrations are per molecule; most are 3 or 6 mM in repeat units. ^bTriplet transfer rate from ³BzPh* to sample. ^cNot measured, Heinzelmann and Labhart⁶⁷ reported value in *n*-hexane, same as oF₁ but missing hexyl side-chains. ^dDetermined based on the extinction coefficient for ³BzPh*. ⁶³ ^eNot measured, value for oF₄ is an average of oF₃ and oF₅, value for oF₆ is scaled between oF₅ and oF₁₀.

Triplet-triplet extinction coefficients and capture rate, k_{TT} . Determination of $T_n \leftarrow T_1$ absorption extinction coefficients, ϵ , were made in benzene for fluorene oligomers, oF_n, of

lengths $n=2-6,10$, polyfluorenes, pF_n , with average lengths of $n=28, 57$ and 84 units, plus two reference molecules. Results are summarized in Table 1. These determinations depend on electron pulse size, which can fluctuate by $\pm 10\%$, corrected by the use of a faraday cup. To provide the most internally consistent and reliable set of extinction coefficients across all samples, individual determinations used an average of 4 shots each, and were further averaged by cycling through all samples, including reference samples, 4-9 times on 1 or 2 different days. Because accuracy of the determinations is best with conditions described in the experimental section, the repeat unit concentrations of oF_n and pF_n used were mostly kept near 3 mM, giving triplet capture times within a factor of about 2 of each other for all lengths. Errors noted are standard deviations of all determinations per sample. Overall accuracy is estimated at $\pm 10\%$, including the reported approximate 4% accuracy of ϵ for the reference, ${}^3Bzph^*$.⁶³

The extinction coefficients for *p*-terphenyl and tetrathiophene determined in this work are also estimated to have small error, $\pm 10\%$, and are well within the ranges previously published. Reports of ϵ for tetrathiophene range widely, from $39,000$ to $75,000$ $M^{-1}cm^{-1}$ in 1,4-dioxane,^{70, 71} with the value determined in the present work in the middle. For *p*-terphenyl values of ϵ are scattered, reported in both benzene ($\epsilon = 90000$ $M^{-1}cm^{-1}$, 460 nm)⁶¹ and hexane ($\epsilon = 75000$ $M^{-1}cm^{-1}$, 440 nm).⁶⁷ Triplet extinction coefficients can depend remarkably on solvent. Bensasson compared $T_n \leftarrow T_1$ absorption spectra of naphthalene and anthracene in cyclohexane and benzene, finding broader and ~ 10 nm red-shifted spectra in benzene accompanied by a 30-50% decrease in the extinction coefficient.⁶¹ This decrease is apparently opposite to that reported for *p*-terphenyl. While the present experiments found the TT spectrum for terphenyl to red-shift in benzene compared to that in hexane, its relatively broad width was not found to be sensitive to solvent (Figure S3, SM). A likely explanation is that the bandwidth is dominated by transient

variations of dihedral angles between phenyl rings in solution which is similar in both solvents, thus samples are likely to have similar extinction coefficient in different solvents. The lack of solvent dependence is expected to be true for all of the molecules in this study, with the effect of dihedrals explored further in the discussion section below.

If, like other properties, $T_n \leftarrow T_1$ extinction coefficients were expected to follow a trend given by the oligomer extrapolation approximation described in the introduction, they would be expected to increase with length to a maximum value, then remain constant for longer oligomers and polymers. Figure 4 plots ϵ versus chain length; lines are added to note trends in the data. We find the expected increase in ϵ for short oligomers, oF₁ - oF₃, however for longer oligomers, ϵ decreases nearly linearly with length, up to 13% by oF₁₀. The shortest polymer tested, pF₂₈, breaks the trend set by oligomers, having only a slightly smaller ϵ than oF₁₀. After this, ϵ continues to drop with a different trend, up to an additional 30% for a polymer ~3x longer. Such decreases in the triplet-triplet extinction coefficient with length are unexpected. The total ~40% drop from oF₃ to pF₈₄ may result in incorrect conclusions in studies where more than 1 length of polymer are compared, or those where polymers have broader length distributions.

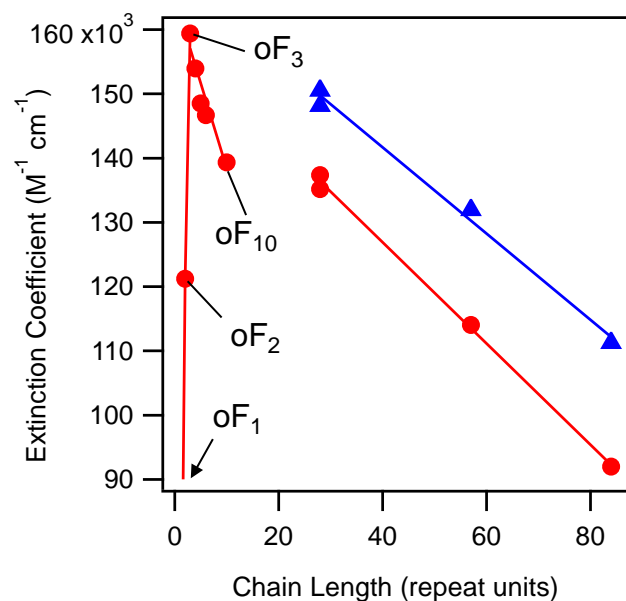


Figure 4. Measured (red circles) $T_n \leftarrow T_1$ extinction coefficients from Table 1 for a series of fluorene oligomers and polymers as a function of average chain length. Corrected (blue triangles) values are described in the Discussion Section. Lines are drawn as a guide.

These measurements also determined the rate constants for triplet transfer (k_{TT}) from $^3\text{Bzph}^*$ to oF_n and pF_n shown in Table 1 and plotted in Figure 5. k_{TT} increases approximately linearly with length, n , but with $k_{TT} \propto 0.44 * n$. This data is similar within experimental error to that previously reported for triplet transfer from $^3\text{biphenyl}^*$ to a narrower range of polyfluorenes with average lengths from 20-80 units, also showing a linear trend.³⁶ The addition of short oligomers in the current work show changes in rate that are consistent with those for longer polymers, and likely are occurring at less than diffusion controlled rates.

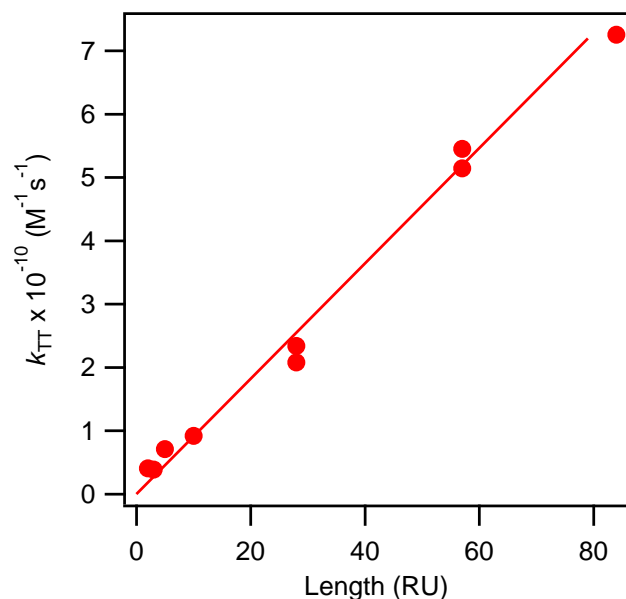


Figure 5. Bimolecular rate constants for triplet transfer from $^3\text{Bzph}^*$ to oF_n and pF_n . The straight-line fit has a growth rate of $0.44 * n$.

IV. DISCUSSION

The oligomer extrapolation approximation might suggest that $T_n \leftarrow T_1$ extinction coefficients, ϵ , oscillator strengths, f_n , and transition dipole moments, μ_n , would all increase to a maximum value at some optimal length, and then remain constant as chain length continued to increase. This optimal length might plausibly be the delocalization length, n_D , of the T_1 state, which is often small.^{27, 29, 49, 52, 53, 72, 73} For oligofluorene triplets, Chen³⁵ reported $n_D = 3.0$ repeat units, which is shorter than delocalization lengths for anions, cations and singlets in the same materials.²² Computations give a similar n_D , with a central dihedral angle of ~ 0 degrees irrespective of oligomer length up to oF_{10} (B3LYP/6-31g(d), Section S5, SM). Results in Table 1 show that extinction coefficients increase from oF_2 to oF_3 , but surprisingly decrease at longer lengths. Figure 3 shows that the oscillator strengths, f_n , and transition dipole moments, μ_n , increase to a maximum near a chain length of 10 units. They appear to follow the oligomer

extrapolation approximation, but with a length of 10, much larger than the triplet delocalization length. The increases of f_n and μ_n to $n = 10$ repeat units, not $n = 3$, occur because the length of the T_n state increases until $n \sim 10$, as suggested in the computed results (Section S5, SM).

If $T_n \leftarrow T_1$ spectral widths were constant, eq 2 predicts f_n to increase proportionately to ε , and eq 3, with correction for position, predicts μ_n to increase as the square root of f_n . That the observed results do not follow of these predictions points to the dominant role of spectral widths. Going from oF_3 to oF_{10} , ε in Figure 4 decreases from 159,400 to 139,300 $M^{-1}cm^{-1}$ (a factor of 1.15). Over the same range Figure S4 (SM) estimates the widths of $T_n \leftarrow T_1$ bands to increase by a factor of 1.99, so the integral in eq. 2 increases by a factor of ~ 1.7 . Thus the increased widths can account for the rise of f_n and μ_n from $n=3$ to $n=10$. By maximizing at 10 units, they suggest that beyond this length the nature of the $T_n \leftarrow T_1$ absorption is unchanged. The shift of the absorption energy seen in Figure 2 stops near 10 units as well, supporting this suggestion. Structural disorder will be identified below as a reason for the increasing width with chain length, as evidenced by the partially resolved vibrational structure in oF_2 becoming blurred out in the longer oligomers. The measured value of the oscillator strength for the shortest polymer, pF_{28} , is 8% smaller than that for oF_{10} . A small amount of motional line narrowing in long polymers compared to short oligomers has been reported to be the result of the exciton exploring a larger region.⁷⁴ If the nature of the $T_n \leftarrow T_1$ transition is unchanged, this would imply larger extinction coefficients, not smaller as we observe. By contrast, we suggest below that the large decreases in $T_n \leftarrow T_1$ extinction coefficient for long polymers has its main root in defects, rather than increases in spectral width observed for oF_3 to oF_{10} .

The striking geometry of the fully relaxed T_1 state, in which just one dihedral angle is driven nearly to zero, might be expected to play an important role in the motion of the triplet on

the chain, and to affect spectra. Analysis below will support the idea that due to triplet motion this structure rarely occurs for chains longer than oF_2 . Previous work assessed this motion finding that triplets generated on pF chains up to 170 units in length moved to end traps with a diffusion coefficient $D \geq 3e-4 \text{ cm}^2/\text{s}$.³⁷ With this minimum value of D , a 1 dimensional hopping model⁷⁵ predicts that a triplet hops by one repeat unit in $\leq 12 \text{ ps}$. Note that this is an *upper* limit for the hopping time, because this value of D was limited by the rate triplets were attached to pF; hopping may be faster than this. If the central dihedral of T_1 can't change to ~ 0 degrees faster than it hops, the chains would adopt a distribution of dihedral angles. Dihedral relaxation times are not known in the current molecules, but insight may be gained based on information from small molecules. Photoexcitation of biphenyl and derivatives produce singlet excited states with flattened central dihedrals, akin to the changes in triplets of oligofluorenes. While Mank reported that dihedral flattening between bare biphenyl rings in cyclopentane may be sub-picosecond,⁷⁶ Lui reported a much slower time constant for an axially substituted biphenyl, 13 ps, in hexane after formation of the singlet excited state, which was slowed further in more viscous solvents.⁷⁷ At the same time, Lui noted that sub-ps decay was largely solvent invariant, concluding it was due to electronic relaxation from higher excited states to S_1 . In the current oligomers and polymers, dihexyl side chains on the 9 position of each fluorene unit likely further slow dihedral flattening to 0° and recovery to $\sim 37.5^\circ$ as the triplet moves along the chain. Other bond length and angle changes are small by comparison and are expected to occur much faster than triplet motion. Jones recently reported similar vibrational and rotational relaxation (flattening) in an octathiophene (T_8) singlet excited state with a lifetime of 11.7 ps.⁷⁸ Again, we expect dihedral changes are likely slower in the current samples, as the T_8 molecules have only 1 hexyl side chain, and lack the steric hindrance present in fluorenes.

From the above, a plausible picture is that triplet motion is too fast for complete flattening and recovery of dihedrals, so the actual geometry in longer oligomers and polymers when a triplet is present may be better described as having more than one partially flattened dihedral angles, depending on the residence time of the triplet in each location. Computations surprisingly found that the delocalization length of the T_1 state, measured from orbitals such as those in Figure S5 (SM), was almost constant when all chain dihedral angles were fixed to average values, and is the same even if all repeat units are held co-planar or at the ground state 37.5 degrees (Figure S6, SM). While dihedral angles larger than 0 degrees only increase the triplet energy up to a few kT , they have a large impact on spectral parameters, increasing f and red-shifting the absorption.

Here we examine the hypothesis, suggested by the computed results, that spectral widths may increase with oligomer chain length due to dynamics. Triplets in oF_2 are immobile; they have a single geometry and therefore a narrow spectrum with partially resolved vibrational structure. In $oF_3 - oF_{10}$ the triplets may move rapidly, encountering varied dihedrals, which broadens the spectra. Increasing inhomogeneous broadening may occur due to the varied solvent environment along longer chains, but this effect is expected to be small.⁷⁴ In polymers with lengths of 28 repeats and longer, the dihedral angles may approach those of chains without triplets also reducing the range of dihedrals and spectral widths. Computations with fully relaxed triplets, which have one dihedral angle near 0° , predict a decrease in oscillator strength, f , from 6 to 10 repeat units, which does not occur in the experiments. This failure of the prediction could be one signal that triplets indeed move too rapidly to allow complete relaxation of dihedrals. The dynamics of dihedral flattening may impact and possibly control triplet transport rates. This

effect was tested by low temperature experiments and a simulation of triplet hopping, described below.

Low temperature. Given the computational prediction that the triplet energy only rises 1-3 kT for a central dihedral angle up to 37.5 compared to the fully optimized 0 degrees, reduced temperature experiments in liquid toluene were expected to be effective at substantially reducing the triplet hopping motion, and possibly locking the triplet into one location on a chain. Figure 6 shows the $T_n \leftarrow T_1$ absorption spectrum of oF₁₀ at both room temperature and -80° C, shifted +650 cm⁻¹ to overlap the peaks. The low temperature spectrum is narrowed by about a factor of 1.8, or 960 cm⁻¹. This narrowing might arise due to a reduction of inhomogeneous broadening from solvent configurations and interactions with the solute. However we see in Figure S7 (SM) that the narrowing over the same temperature range is less than half as large for oF₂. We suggest that the ~400 cm⁻¹ reduction in broadening for oF₂ at low temperature gives a measure of the reduction of inhomogeneous broadening due to the solvent common to both molecules, while the additional decrease seen in oF₁₀ reflects a reduction and possibly elimination of triplet hopping. In oF₂, there is only a single dihedral, so the triplet is stationary, and the dihedral will be nearly flat regardless of temperature. The hypothesis above implies that triplets move in longer chains, resulting in a range of dihedral angles that have varied absorption energies, giving broad spectra. At low temperature, the oF₁₀ triplet is likely frozen in mostly a single location, lacking the thermal energy necessary to rapidly hop to less energetically favorable locations on the chain. This allows the dihedral where the triplet is located to become flat like those in oF₂, and results in a narrower absorption spectrum due to a lack of the different geometries present at room temperature.

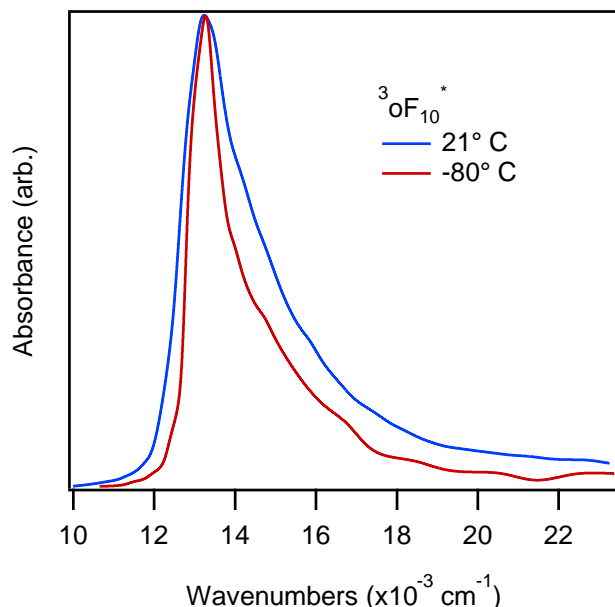


Figure 6. $T_n \leftarrow T_1$ spectrum of oF_{10} at 21 °C and -80 °C (shifted +650 cm^{-1} from its spectrum with a max at 12630 cm^{-1}). Spectral FWHM bandwidths are 2203 and 1240 cm^{-1} respectively.

Hopping Simulation. To get a sense of how the competition between hopping and dihedral relaxation might alter $T_n \leftarrow T_1$ spectra we constructed a simple simulation program aimed to simulate distributions of dihedral angles created by triplet hopping. The simulation used the ratio of rate constants for hopping and dihedral propagation, $k_{\text{hop}} / k_{\text{dih}}$ as the key parameter. The source C-code and detailed explanations are given in Section S8 (SM). The resulting distributions of dihedral angles were summed over 1000 simulations to provide average values. The decision to hop was made without regard to the change in T_1 free energy for which we have no method to give an accurate estimate, however is expected to be small ($< k_bT$) based on idealized B3LYP/6-31G(d) calculations where dihedrals were changed by small amounts. Inclusion of this effect might tend to narrow distributions, depending on k_{hop} and k_{dih} , but in most results below, this was a small effect because the distribution of angles is broad. Figure 7 shows

simulation results at different ratios, $k_{\text{hop}}/k_{\text{dih}}$ for oF₆, displaying a general trend common to all lengths. Results for other lengths are given in Figure S9 (SM).

For slow hopping, $k_{\text{hop}} \ll k_{\text{dih}}$, the simulations find that only one dihedral is flat, while all of the others are near 37.5 degrees. This intuitively-expected result is the same as predicted by computations of fully relaxed triplets on oligofluorene chains discussed above, giving very short triplets. As the hopping rate increases, we see the development of a range of dihedral angles, having a maximum width when k_{hop} is 30 times k_{dih} for oF₆. At higher hopping rates, the range of dihedral angles *decreases*, with a peak value for each oF_n equal to $37.5 \cdot (n-1)/n$. For oF₆, this most probable dihedral angle becomes 31 degrees at high $k_{\text{hop}}/k_{\text{dih}}$. This behavior is expected for very fast transport where the triplet visits every site on the chain many times and dihedral rotation is slow by comparison, resulting in most dihedrals averaged to the same angle. In long chains such as oF₂₀ (Fig. S9, SM) the distribution of angles for $k_{\text{hop}}/k_{\text{dih}} \geq 1$ is truncated at close to 37.5 degrees, resulting in narrower distributions, consistent with the suggestion above that long chains may have little geometry change from neutral polymers.

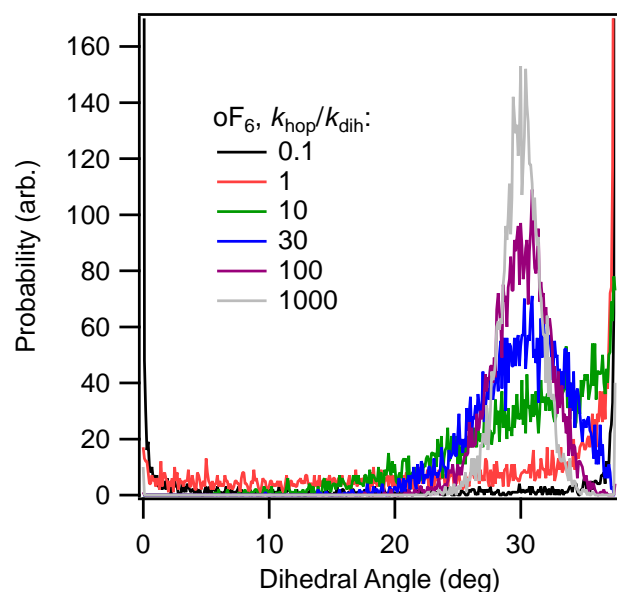


Figure 7. Probabilities of dihedral angles from 0-40° for oF₆ in a hopping simulation. Traces are labeled with the ratio of the hopping to dihedral propagation rate, $k_{\text{hop}}/k_{\text{dih}}$, from 0.1 to 1000.

The results establish that for fast hop rates, triplets on polyfluorene chains produce a much wider range of dihedral angles than predicted for a fully relaxed and stationary T₁ state, and that the range of angles depends on oligomer length. Broader dihedral distributions will lead to broader T_n ← T₁ absorption spectra. Spectral widths from broadened distributions were estimated using sums of computed absorptions for different dihedral angles in Section 10 of the SM. The present simple model qualitatively reproduces the experimental width dependence of triplet spectra with chain length best when the ratio $k_{\text{hop}}/k_{\text{dih}}$ is between 30-100. While the model is not quantitative, it is of interest to note what this ratio might imply about k_{hop} and k_{dih} . Using the upper limit for the triplet hopping time of 12 ps derived above from the published minimum value of D ,³⁷ one might predict a dihedral relaxation time of 0.4-1.2 ns. This is very slow compared to the 12-13 ps relaxation time reported by Jones or Liu discussed above.^{77, 78} The current molecules are much larger and have bulky side-groups that will make dihedral torsions slower, but it might be surprising if they slowed to this extent implying that hopping might be faster than reported $D \geq 3\text{e-}4 \text{ cm}^2/\text{s}$.³⁷ In any case, results of the simulations paint a picture in which triplets transport faster than dihedrals can fully respond, likely fast enough that the idealized picture of the T₁ state with one flat dihedral is rare. Instead dihedral angles have broad distributions in oligomers and are nearly unchanged in longer polymers molecules from the starting ground state geometry.

Polymer Defects. The discussion above concluded that decreases in extinction coefficient with increasing length for oligomers and short polymers is due to increases in spectral width that overcome increasing oscillator strength, f , to 10 units long,. These factors cannot explain the apparent decreases of extinction coefficients in Figure 4 observed in longer pF₂₈ - pF₈₄ chains. These decreases can be explained by defects in polymer chains and could provide estimates of the prevalence of defects. Triplets are expected to be very sensitive to defects, which may act as simple barriers to triplet motion, sites where they become immobilized or sites where triplets are either destroyed or changed into new species that absorb at different wavelengths. Defects are expected to occur randomly, with a likelihood proportional to chain length. Keto defects particularly for mono-alkylated polyfluorenes have been reported to trap charges and excitons, resulting in green emission.^{79, 80} Green emission has not been detected in the current materials,⁴⁸ so any defects are likely of a different type. The fast triplet diffusion in polyfluorenes reported in previous work, with $D \geq 3e-4 \text{ cm}^2/\text{s}$,³⁷ predicts that triplets explore the entire chain many times within the triplet lifetime, and thus will find a defect if present. For defects to affect measured extinction coefficients, they must result in loss of polyfluorene triplets.

To seek evidence of such a loss of triplets due to defects, we transferred pF triplets to 0.3 mM anthracene (An) in solutions containing 200 mM benzophenone with 0.21 mM pF₅₇ (12 mM in repeat units). Most triplets are captured first by pF₅₇, then transferred to An. Detailed analysis and figures are shown in Section S11 (SM). The ratio of ³An* made with and without pF₅₇ is 0.864, indicating that 13.6% of polymer chains experience loss of the triplet, plausibly due to the presence of one or more defect. Because only this ratio is needed, interpretation of this experiment required no knowledge of extinction coefficients. With 13.6% of the triplets lost to defects the ³pF_n* extinction coefficients in Table 1 are too small.

A binomial distribution defect rate of 1 in 586 polymer repeat units was estimated considering the actual length distribution of chains in the pF₅₇ sample as shown in Figure S12 (SM). Note that in pF_n samples, there are more chains longer than the average length than chains that are shorter. Longer chains are more likely to have defects and will also capture triplets at higher rates as seen in Figure 5. This defect rate is consistent with a rough estimate given in previous work of less than 1 destructive defect in 500 repeat units based on triplet transport to end-cap trap groups, however this estimate did not consider length distributions.³⁶ Armed with defect rates, Table 2 gives fractions of polymer chains in pF₂₈-pF₈₄ with defects, f_d , and makes corrections to the pF_n extinction coefficients in Table 1, $\underline{\epsilon}_d$. The corrected extinction coefficients are 7-20% higher than those in Table 1. We assumed that the oligomers, which were synthesized by a different route, have no substantial defect rate.

Table 2. Corrections to pF_n T_n ← T₁ extinction coefficients due to defects. Errors are +/- 10%.

<u>Sample</u>	<u>[S] (mM)</u>	<u>f_d^a</u>	<u>ϵ_d (M⁻¹ cm⁻¹)^b</u>	<u>r_d^c</u>
pF ₂₈	0.11	0.0876	148100	1/1790
pF ₂₈	0.21	0.0876	150500	1/3760
pF ₅₇	0.11	0.136	132000	1/424
pF ₈₄	0.036	0.173	111300	1/263

^aFraction of chains with a defect using the distribution of chain lengths and a binomial distribution. ^bRevised extinction coefficient taking f_d into account. ^cDefect rate per repeat unit needed to make extinction coefficient the same as oF₁₀.

Extinction coefficients for ${}^3\text{pF}_n^*$ corrected for defects, ϵ_d , are plotted in Figure 4. The corrected value for pF_{57} is about 5% smaller than that for oF_{10} , within the overall 10% experimental error described in Results. The corrected ϵ_d , based on triplet transfer to anthracene, still decreases with chain length for pF_{28} - pF_{84} , with a slope nearly the same as for uncorrected values. The reason for this is not clear, nor is the nature of the traps. The discussion above assumes that traps kill triplets or move them to a defect with a low enough triplet energy that they cannot transfer to anthracene. One possible issue may be the latter type of defect if they have a triplet absorption at the same wavelength as ${}^3\text{pF}^*$. These would result in extinction coefficients that are too low, however would not change the slope appreciably. If a chain attaches more than 1 triplet, triplet-triplet annihilation would lead to underestimations of $T_n \leftarrow T_1$ extinction coefficients. This effect would be most pronounced in the longest polymers, producing smaller apparent ϵ with increasing length. At the low concentration of triplets made, fewer than 1% of chains attached more than 1 triplet, so annihilation is insignificant. If we assume that ϵ_d should be constant for chains longer than 10 units, a likely explanation for pF_n results is that the defect rate per repeat unit is not constant, but rather is proportional to chain length. This would require the defect rates, r_d , shown in Table 2 to match ϵ for oF_{10} . These values predict a linear growth of defect rate per repeat unit with polymer length. This might be a result of the polymer synthesis, where longer chains have vulnerable active growth sites for longer times than short ones.

V. CONCLUSIONS

Extinction coefficients, ϵ , are reported for $T_n \leftarrow T_1$ absorptions in a set of oligo- and poly-fluorenes. Together with measured spectra these give oscillator strengths and transition moments that level off after rising smoothly from 2 to 10 fluorene repeat units, thus following the oligomer extrapolation approximation. The extinction coefficients themselves do not follow this trend. Their fall from a maximum at oF_3 to oF_{10} is due to spectral broadening, much of which arises from a distribution of dihedral angles because triplet hopping along chains competes with dihedral relaxation. Application of an elementary model of this competition yields the conclusion that triplets diffuse so fast along chains that dihedral relaxation does not keep up in accord with earlier observations of the triplet diffusion coefficient, $D \geq 3 \times 10^{-4} \text{ cm}^2/\text{s}$.³⁷

At low temperature, the triplet is expected to move very slowly, so the T_1 state is delocalized over ~ 3 units independent of chain length, with a 0° central dihedral angle in accord with the structure optimized by computation. That 0° dihedral would be rare in chains at room temperature. At low temperatures spectral widths might not increase with oligomer length. For triplets in long polymers, dihedral angles may not differ significantly from the $\sim 37.5^\circ$ in ground state, as the triplet does not spend enough time in any one location for the low temperature geometry to develop, as suggested by the simple computer simulation described here.

SUPPLEMENTARY MATERIAL

The Supplementary Material contains: Steady-state absorption spectra; details for pulse radiolysis data fitting; analysis of the empirical $1/n$ fit of data in Figure 2; comparison of $T_n \leftarrow T_1$ (TT) absorption spectra in benzene and hexane; TT absorption spectra widths on an

energy axis; orbitals for TT transitions for optimized triplets on oF₂-oF₁₀; impact of central dihedral angle on T₁ delocalization length; -80 °C TT spectrum for oF₂; source C code and explanation for hopping simulation; distribution of simulated dihedral angles for oF₃-pF₂₀; connection of dihedral angle to TT absorption energy; modeling of raw data for defect rate determination; chain length distribution in the pF₅₇ sample.

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