

Ultrafast Dynamics in Multifunctional Ru(II)-Loaded Polymers for Solar Energy Conversion

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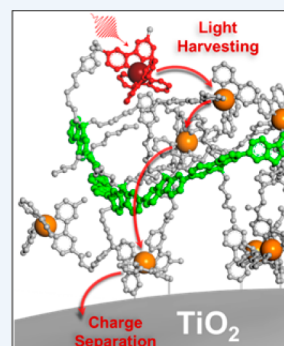
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CONSPECTUS: The use of sunlight to make chemical fuels (i.e., solar fuels) is an attractive approach in the quest to develop sustainable energy sources. Using nature as a guide, assemblies for artificial photosynthesis will need to perform multiple functions. They will need to be able to harvest light across a broad region of the solar spectrum, transport excited-state energy to charge-separation sites, and then transport and store redox equivalents for use in the catalytic reactions that produce chemical fuels. This multifunctional behavior will require the assimilation of multiple components into a single macromolecular system.

A wide variety of different architectures including porphyrin arrays, peptides, dendrimers, and polymers have been explored, with each design posing unique challenges. Polymer assemblies are attractive due to their relative ease of production and facile synthetic modification. However, their disordered nature gives rise to stochastic dynamics not present in more ordered assemblies. The rational design of assemblies requires a detailed understanding of the energy and electron transfer events that follow light absorption, which can occur on time scales ranging from femtoseconds to hundreds of microseconds, necessitating the use of sophisticated techniques. We have used a combination of time-resolved absorption and emission spectroscopies with observation times that span 9 orders of magnitude to follow the excited-state evolution within polymer-based molecular assemblies. We complement experimental observations with molecular dynamics simulations to develop a microscopic view of these dynamics.

This Account provides an overview of our work on polymers decorated with pendant Ru(II) chromophores, both in solution and on surfaces. We have examined site-to-site energy transport among the Ru(II) complexes, and in systems incorporating π -conjugated polymers, we have observed ultrafast formation of a long-lived charge-separated state. When attached to TiO₂, these assemblies exhibit multifunctional behavior in which photon absorption is followed by energy transport to the surface and electron injection to produce an oxidized metal complex. The oxidizing equivalent is then transferred to the conjugated polymer, giving rise to a long-lived charge-separated state.



■ INTRODUCTION

Multifunctional molecular and macromolecular assemblies that are able to harvest light, separate charge, and utilize the resulting redox equivalents to drive solar fuels reactions are an integral component in many artificial photosynthetic strategies.^{1,2} Multifunctional behavior is achieved through a combination of fundamental energy and electron transfer events. While both of these processes have been extensively characterized in simple, well-defined systems consisting of only a few (often only two) molecular components, the structural complexity arising from the integration of multiple components leads to dynamical phenomena that are not found in dyads and triads. Thus, functionality in artificial assemblies cannot be understood through studies of individual components or small model systems.

The characterization of dynamical phenomena (e.g., charge and energy migration) in large polymer-based assemblies is a challenging problem. Transport phenomena, for example, depend upon the macromolecular structure, which in turn depends upon the polymer support and the chemical structure of the monomer. The spatial relationship of the monomer's excited-state wave function to other assembly components, rigidity of the polymer, solvent polarity, and the nature of the counterion can influence the structure and affect the exciton dynamics. In large macromolecular systems,^{3–13} the separation between adjacent components is described not by a single distance but rather by a distribution of distances that, in turn,

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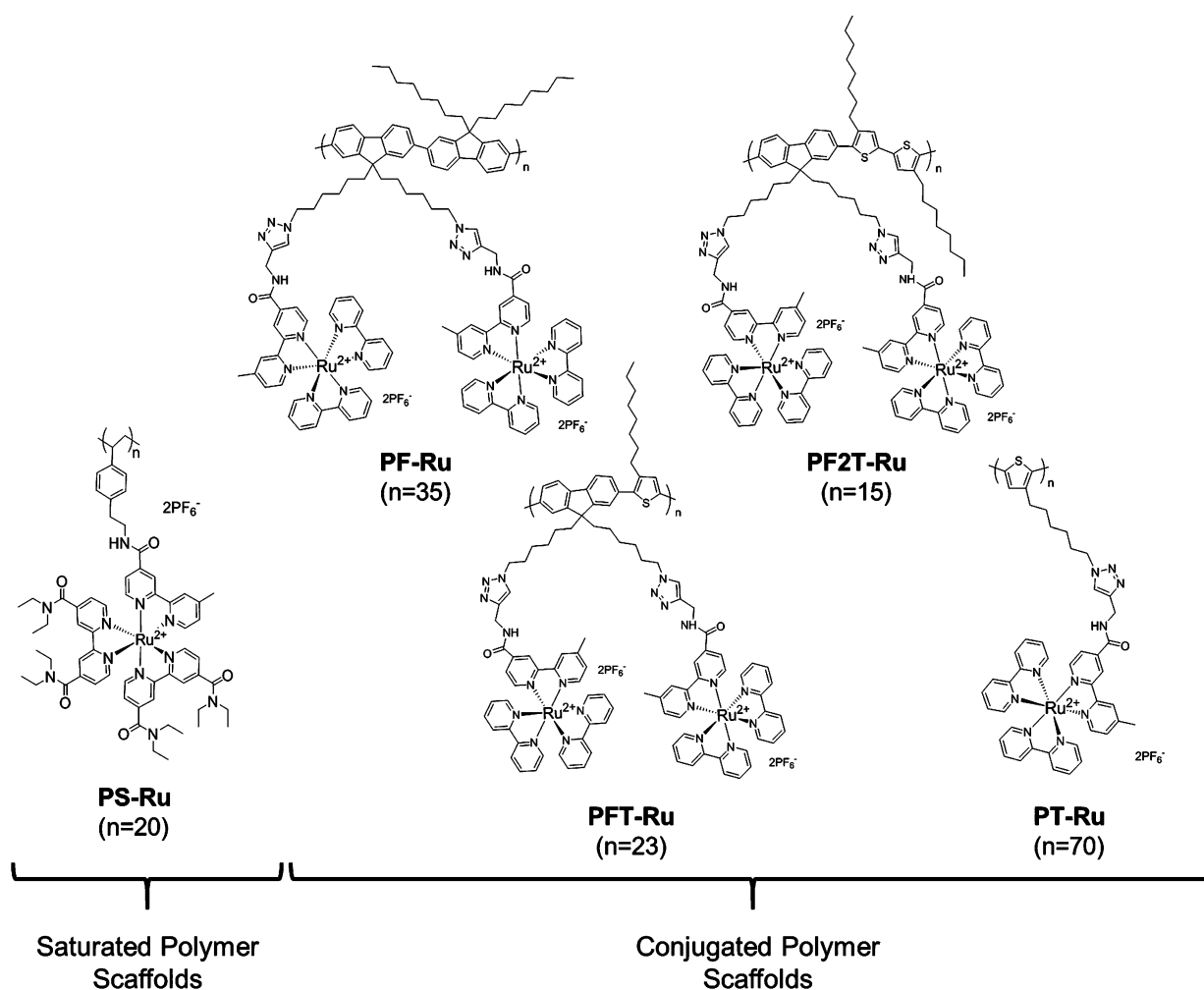


Figure 1. Chemical structures of polymer assemblies consisting of either saturated (PS-Ru) or π -conjugated backbones (PF-Ru, PFT-Ru, PF2T-Ru, and PT-Ru). The variable n refers to the average length of the polymer backbones.

results in a distribution of electron and energy transfer rates. Furthermore, the presence of flexible linkages can give rise to large-scale conformational motions that can occur on time scales similar to the transfer rates,¹⁴ leading to rate constants that may be more influenced by molecular motions than the quantities normally associated with electron and energy transfer, including electronic couplings, reorganization energies, and driving forces.¹⁵ Thus, even the relatively simple process of site-to-site energy transport will exhibit highly nonexponential kinetics, and disentangling contributions from the various dynamical phenomena can oftentimes only be accomplished through the use of sophisticated simulations and modeling to extract intrinsic rates from experimental data.

In this Account, we focus on the ultrafast dynamics of polymeric assemblies consisting of multiple Ru(II) polypyridyl complexes linked together by a polymer backbone (Figure 1). We have used a combination of ultrafast spectroscopic methods and computer simulation (Monte Carlo and molecular dynamics) to characterize the fundamental photophysical processes that take place on time scales ranging from several hundred femtoseconds to hundreds of microseconds. Early work from our laboratory focused on light-harvesting assemblies utilizing poly(styrene) (PS) as the scaffold.^{4,16–19} The electronic states of the polymer lie at higher energy, and as a result, visible excitation occurs at the pendant metal

complexes. The PS serves only a structural function, holding the metal complexes in close proximity to one another to facilitate excited-state transport. More recent work has explored assemblies based on π -conjugated polymers.^{20–22} Here, not only does the polymer serve as a structural support, but because of its strongly allowed $\pi \rightarrow \pi^*$ transitions, it can also function as a secondary light-absorbing component.

Excitation of the polymer results in either energy transfer to the pendants or electron transfer from the polymer to one of the pendant metal complexes, producing a charge-separated state that persists from nanoseconds to microseconds. Multifunctional behavior is readily apparent in PF-Ru assemblies attached to TiO₂. With the use of transient absorption spectroscopy across a broad range of time scales, we observe light harvesting by the pendant complexes, charge separation at the interface, and transfer of the oxidative equivalents to the backbone, resulting in a charge-separated state that persists for several hundreds of microseconds.

■ POLYMER STRUCTURES

The fundamental photophysical processes of energy and electron transfer that take place in these complex assemblies depend on the separation and relative orientation of the individual components. The macromolecular structure is determined by a number of factors, including the torsional

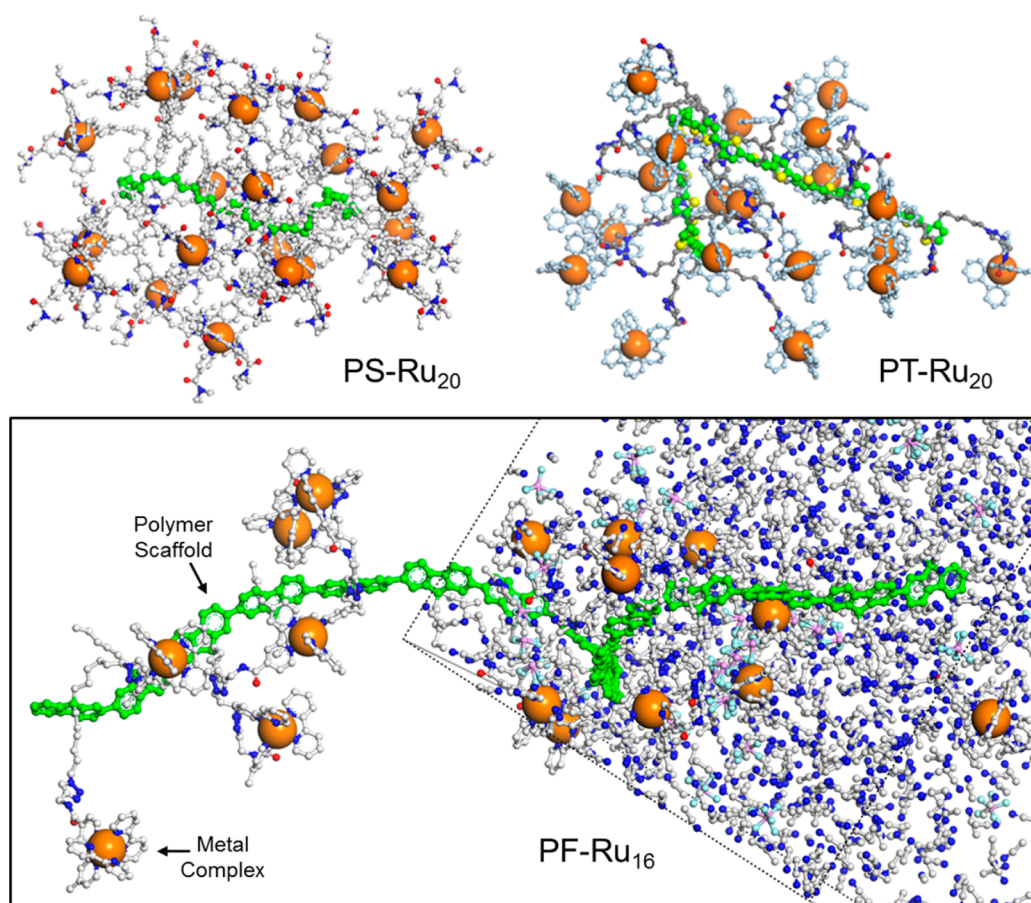


Figure 2. Condensed phase polymer assembly structures obtained from molecular dynamics simulations. Structures were calculated using periodic boundary conditions in the presence of explicit acetonitrile solvent and PF_6^- counterions. The polymer scaffold is shown in green color, and the Ru atoms are depicted as orange spheres with enlarged diameters. A portion of the solvent is shown in the PF-Ru₁₆ structure.

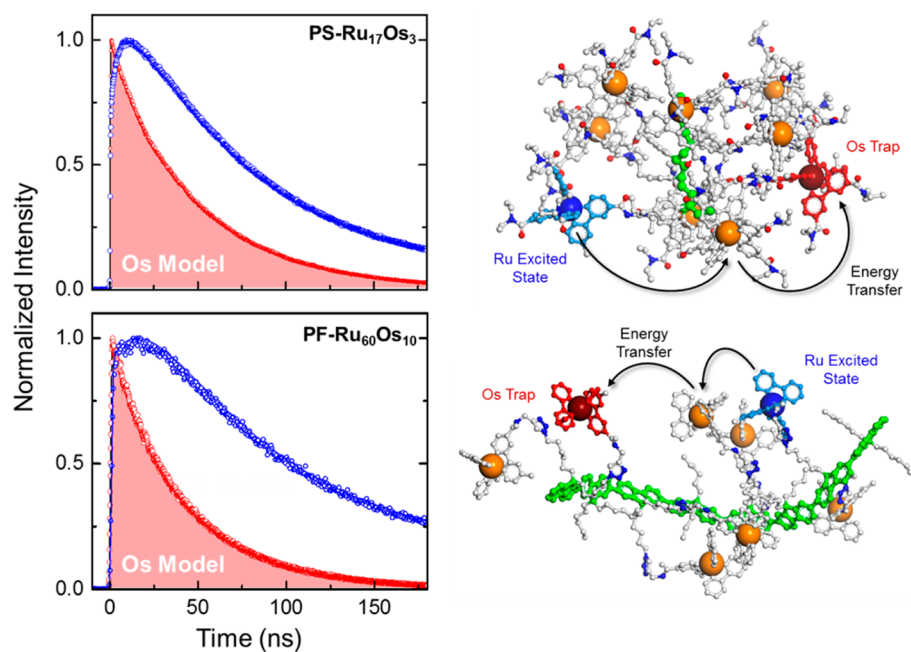


Figure 3. (left) Time resolved emission monitoring Os(II) photoluminescence in PS-Ru₁₇Os₃ and PF-Ru₆₀Os₁₀. (right) Illustration of site-to-site energy transport within a subsection of PS-Ru₁₇Os₃ (upper) and PF-Ru₆₀Os₁₀ (lower). The initial Ru excited state (blue) undergoes energy transfer to adjacent Ru complexes and is ultimately transferred to the Os trap (red).

flexibility of the backbone, the size and spacing of the pendant groups, the length of the side chains, and the solvent, which vary among the five different assemblies shown in Figure 1. In PS-Ru, for example, each repeat unit of the polymer scaffold is functionalized by a metal complex that is connected to the backbone by a short side chain (Figure 2). This dense chromophore loading combined with the flexible nature of the poly(styrene) causes significant twisting of the polymer backbone in order to accommodate the large pendant metal complexes. Monte Carlo and molecular dynamics simulations indicate that the structure is close-packed, with each complex lying within 2–3 Å of its neighbors.⁴ Whereas the macromolecular structure of the PS-Ru system is determined primarily by steric considerations and packing, the poly(fluorene)-Ru (PF-Ru) and poly(thiophene)-Ru (PT-Ru) structures are more heavily influenced by intramolecular and intermolecular forces (Figure 2). The conjugated π -network present in PF and PT reduces the torsional flexibility of the scaffold, resulting in more extended structures, and this combined with the significantly longer side chains leads to larger average separations between adjacent complexes compared with PS-Ru. Solvent can also play a significant role, particularly in the more open PF-Ru and PT-Ru systems. Polar solvents have favorable interactions with the pendant complexes but not the polymer backbone, and as a result the assembly may adopt a structure where the side chains extend out into the solvent or one in which the metal complexes take positions near the polymer to shield it from the more polar environment.

■ SITE-TO-SITE ENERGY TRANSPORT

Site-to-site energy migration is initiated through metal-to-ligand charge transfer (MLCT) excitation of one of the pendant Ru(II) complexes. The singlet MLCT state decays rapidly into a long-lived triplet MLCT, whose lifetime can extend from hundreds of nanoseconds to microseconds.²³ Because of the close proximity of the neighboring complexes, Ru* excitation migrates along the chain in a random-walk like fashion through a series of isoenergetic triplet–triplet (i.e., Dexter) energy transfer events between adjacent complexes. Energy transport is observed by replacing a small fraction of the Ru sites with Os(II) complexes, that is, PS-Ru₁₇Os₃ and PF-Ru₆₀Os₁₀. Because the Os sites have a lower energy excited state, they serve as traps that terminate the site-to-site random walk.^{4,16–18} Thus, photoexcitation of the Ru sites is followed by a delayed rise in the Os* emission, which is a clear signature of the transport of excited-state energy to the Os traps (Figure 3). (Note that the instantaneous rise in the emission intensity at $t = 0$ is not the result of Ru* \rightarrow Os energy transfer, but rather reflects a combination of emission resulting from both direct excitation of the Os sites and weak Ru emission that is also detected at the monitored wavelength, \sim 780 nm).

The energy transport process includes a series of Ru* \rightarrow Ru hops followed by a terminating Ru* \rightarrow Os energy transfer event. The growth in the Os* emission reflects the *total* time for this process and thus reflects both the hopping time (τ) and the number of hops needed to reach the trap. The latter depends upon the fraction of Os sites; the greater the Os loading, the fewer the number of hops needed and the faster the rise in the photoluminescence intensity. Thus, while the growth indicates the presence of energy transport, the rise time itself is not a direct measure of the intrinsic Ru* \rightarrow Ru hopping time.

Stochastic kinetic simulations provide a means of extracting the microscopic details of energy transport from the experimental data. The first step involves determining the macromolecular structure of the assembly using Monte Carlo simulation methods.⁴ A structure is selected from the ensemble, and each site is assigned to be Ru or Os according to the loading statistics. One of the Ru sites is selected as the initial location of the excited state and energy transfer rate constants (k_{EnT}) are calculated to its nearest neighbors using a Dexter formalism, that is, $k_{\text{EnT}}(R) = k_0 \exp(-\beta R)$, where R is the separation between sites, k_0 is the rate constant at closest contact, and β is an attenuation parameter that determines the falloff of the electronic coupling with distance.¹⁵ Because the chemical linkage connecting adjacent complexes contains a significant number of saturated carbons, the electronic coupling between sites arises primarily from direct orbital overlap between the donor and acceptor complexes. In this limit, β is \sim 1–2 Å⁻¹, making energy transfer extremely short-range.

Energy migration “trajectories” are propagated using a stochastic kinetic algorithm. The simulation averages many trajectories, each obtained by sampling different structures and loading configurations, to produce an output that is “fit” to the experimental data in an *ad hoc* fashion.²⁴ The simulations of energy transport in the PS-Ru₁₇Os₃ assembly reveals a distribution of hopping times ($\tau_{\text{avg}} = 1–3$ ns) with a broad distribution in the number of hops needed to reach the Os trap.

The wide variation in the number of hops needed to reach an Os site is (in part) a reflection of the significant chain-to-chain variation in the Os loading. The fraction of Os sites in PS-Ru₁₇Os₃ is 15%, but this represents an average of the entire ensemble of chains. We estimate that only a quarter of the chains have three Os complexes, while many (\sim 20%) have only one or none, and about 10% have six or more. For chains with a large fraction of Os sites, the number of hops needed to reach the trap may be as small as 2–3, but for chains with only a single Os site it may take tens or even hundreds of hops. The presence of migration trajectories with a large number of Ru* \rightarrow Ru hops is suggested by the persistence of sensitized Os emission 200–400 ns after excitation, well beyond the \sim 50 ns excited-state lifetime of the Os complex (Figure 3).

The energy transfer times observed in the PS-Ru₁₇Os₃ assembly (1–3 ns) are long compared with singlet–singlet (i.e., Förster) energy transfer times observed in many systems.^{25–27} Despite the slower energy transfer time, the transport of the excited state to the Os trap sites is extremely efficient. We estimate that about 95% of the Ru* excited states created on polymer chains with at least one Os complex are eventually transported to a trap site. The high transport efficiency in the PS-Ru assembly stems in part from the dense packing of the metal complexes, which ensures that a Ru* excited state is always in close contact with one of its neighbors. While this dense packing is important, the long lifetime of the Ru* excited state (\sim 1 μ s) also plays a role. Thus, even though the energy transfer time is long (1–3 ns), it is fast compared with the Ru* lifetime, suggesting that the efficiency of a single energy transfer step is greater than 99.7%.

Transient photoluminescence data collected from the PF-Ru₆₀Os₁₀ assembly also exhibits the delayed rise in the Os* emission that is characteristic of site-to-site transport (Figure 3). Compared with PS-Ru₁₇Os₃, the slower rise is suggestive of a longer time scale for energy transport. While we have not yet performed Monte Carlo simulations on this system, analysis of the emission spectra suggests \sim 80% of the Ru* excited states

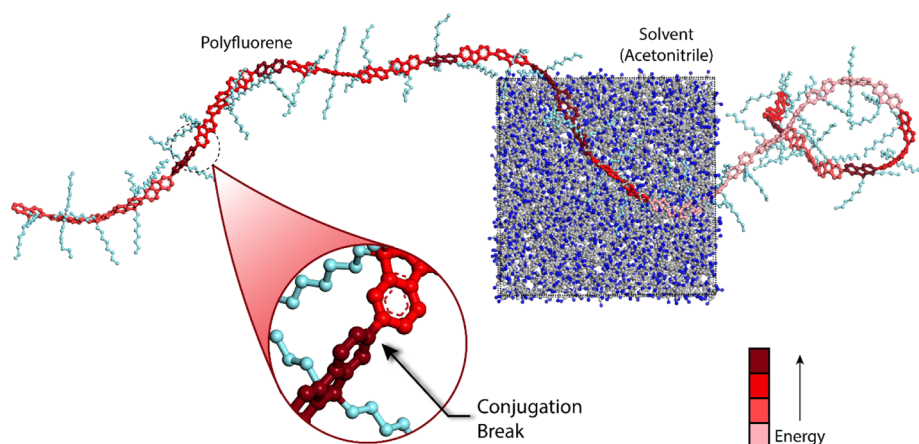


Figure 4. Condensed phase structure of a 40-repeat unit PF in explicit acetonitrile solvent obtained from molecular dynamics simulations. Most of the solvent is omitted for clarity, but a portion is shown for scale. The conformational subunits are colored based on the energy level with darker shades indicating subunits with shorter lengths and hence higher energies. The enlarged section shows a zoomed-in view of adjacent conformational subunits with a conjugation break.

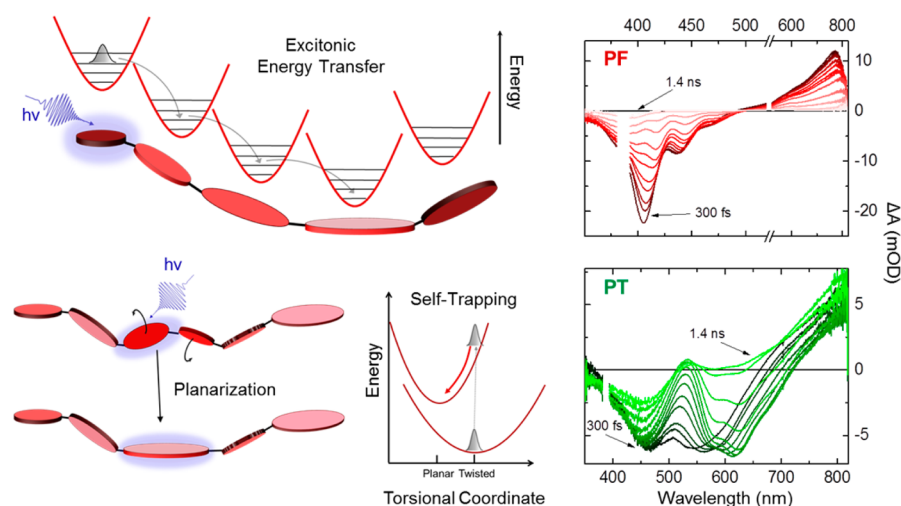


Figure 5. (left) Illustration of excitonic energy transfer (top) and excited-state self-trapping by torsional relaxation (bottom) along a π -conjugated polymer backbone following excitation into a high-energy conformational subunit. (right) Transient absorption difference spectra of unfunctionalized PF (upper) and PT (lower) from 300 fs to 1.4 ns following 388 nm excitation.

produced by photoexcitation are transferred to one of the Os sites. This relatively high efficiency is remarkable, especially given the low packing density of the metal complexes compared with PS-Ru₁₇Os₃ (Figure 3) and the close contact needed for triplet–triplet energy transfer. The high efficiency observed in the PF-Ru₆₀Os₁₀ assembly may be an indication that energy transport is facilitated by the conformational fluctuations that bring two complexes into close proximity where the short-range triplet–triplet energy transfer is possible. If this is the case, then one would anticipate that solvent viscosity could have a dramatic effect on the dynamical behavior when the chromophore density gives rise to large separations between complexes.

Conformational flexibility may not only help overcome the limitations of short triplet–triplet energy transfer distances but also mitigate effects of energetic disorder. The highly charged nature of the polymer and corresponding counterions gives rise to a heterogeneous electrostatic environment that lifts the degeneracy of neighboring sites. The lower energy sites act as shallow traps that impede energy transport. In fluid solution, like the examples discussed above, conformational motion is

constantly changing this environment, and the effects of energetic disorder are masked. When polymer assemblies are dispersed in rigid matrices, this conformational motion is frozen out on the time scale of energy hopping. As a result, energy transfer is biased toward lower energy, and once the lowest energy sites are reached, transport of the excited state slows considerably.²⁸ Transient photoluminescence experiments performed on assemblies embedded in rigid environments show evidence of the loss of conformational flexibility. Whereas emission spectra in fluid solution show little (or no) time-dependent shift in the band position, experiments on PS-Os₂₀ exhibit a clear red shift in the emission band with increasing time after excitation that results from this energetic disorder.¹⁷ The exploitation of conformational flexibility could be a powerful design concept in the development of multifunctional assemblies.

■ COMPETITIVE CHARGE SEPARATION AND ENERGY TRANSFER

In assemblies utilizing π -conjugated polymers, photoexcitation of delocalized $\pi \rightarrow \pi^*$ transitions in the visible gives rise to

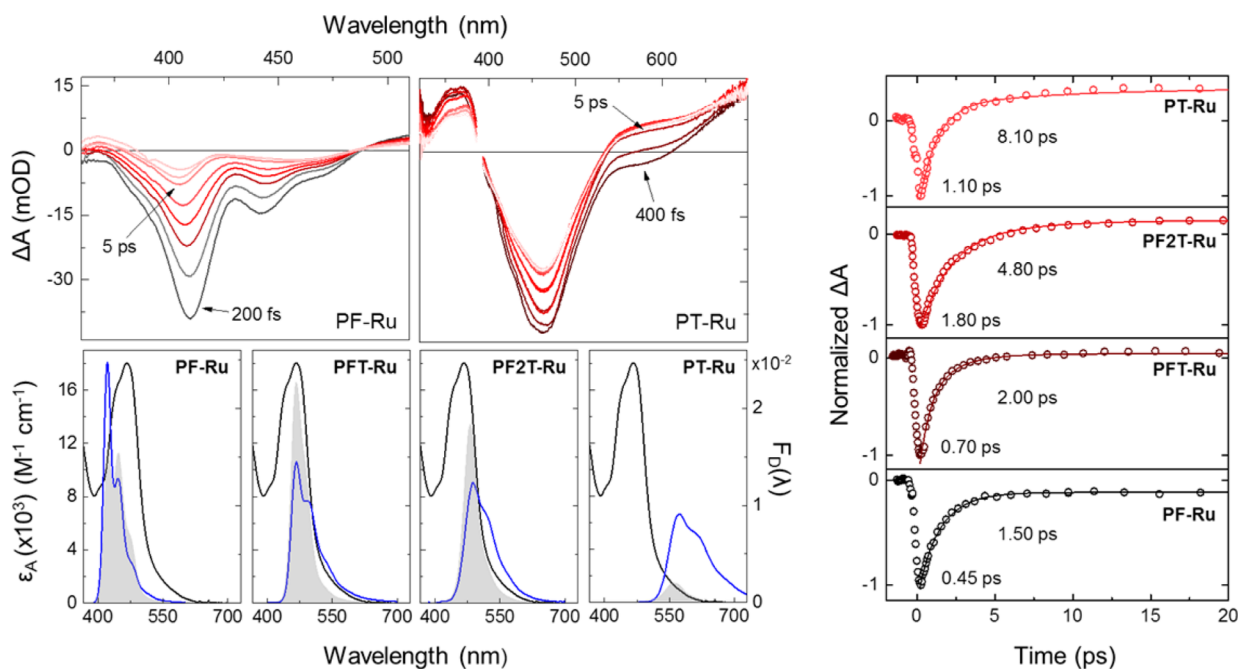


Figure 6. (left, top) Transient absorption difference spectra following primary excitation of the polymer backbone at 388 nm for PF-Ru (upper left) and PT-Ru (upper right). (left, bottom) Ru(II) absorbance ($\epsilon_A(\lambda)$) and normalized (to unit area) polymer emission spectra ($F_D(\lambda)$). The shaded gray area reflects the integrand, $F_D(\lambda)\epsilon_A(\lambda)\lambda^4$, which is scaled for clarity. (right) Kinetic traces of the polymer assemblies showing the initial polymer excited-state quenching during the first 20 ps following excitation.

additional dynamical phenomena. The excited-state dynamics of conjugated polymers have been studied extensively, both in solution and as thin films.^{29–33} Conformational disorder breaks up the conjugation along the backbone as a result of relatively low energy barriers for bond rotations between subunits, resulting in a chain of linked chromophores of varying conjugation lengths,^{34,35} as depicted in the PF structure in Figure 4. The final structure is an energetic compromise between the entropic gain associated with producing a disordered structure and the energetic destabilization that occurs upon breaking the conjugation. The broad absorbance spectrum of the solvated polymer is a manifestation of this disorder, with longer conjugation lengths contributing to the red edge of the spectrum and shorter to the blue.³³

Photoexcitation of PF and PT polymers results in a rich set of dynamical phenomena. On very short time scales (<100 fs), coupling of the excitation to small-scale torsional motions causes rapid relaxation and localization of the exciton onto a small number of monomer units.^{31,36} Transient spectra obtained on longer time scales from PF and PT (i.e., unfunctionalized) chains in solution are dominated by a series of negative-amplitude features in the blue that arise from a combination of ground-state bleach and stimulated emission, as well as a low-energy absorption associated with the singlet excited state of the polymer (Figure 5). The stimulated emission bands decay in amplitude (due to excited-state relaxation) and shift to lower energy with increasing time. The red shift is indicative of torsional relaxation or exciton migration.^{31,33,37,38} In PF, the stimulated emission shifts a few nanometers over several hundreds of picoseconds, due to a combination of large-scale conformational rearrangements and intrachain energy transfer to lower energy sites (Figure 5).^{31,32} In PT, the spectral changes are much more extensive, reflecting slow torsional relaxation that results in large-scale planarization of the backbone, such that by 100 ps, the fully relaxed excitons

are formed. It has been previously shown that additional exciton stabilization is achieved through the presence of strongly coupled low-frequency torsional degrees of freedom,³⁹ which is consistent with the greater spectral evolution (Stokes shift) observed in PT compared with PF. In both PF and PT, the exciton decays through either emission or intersystem crossing to form longer-lived triplet excitons.^{30,31}

The transient spectra obtained from PF-Ru following excitation of the PF backbone are dramatically altered by the presence of the pendant Ru complexes (Figure 6). The stimulated emission feature observed at early times resembles that seen in PF, but in PF-Ru it is quenched within several picoseconds. The transient spectra are also qualitatively different. Whereas in PF the stimulated emission shifts continuously to the red, in PF-Ru this band initially shifts to the red, but after a few picoseconds shifts back to higher energy. This behavior is the result of PF* quenching through a combination of energy and electron transfer mechanisms. Energy transfer to give a singlet Ru excited state (i.e., ${}^1\text{PF}^* + \text{Ru}^{2+} \rightarrow \text{PF} + {}^1\text{Ru}^{2+*}$) occurs with a time constant of 450 fs, accounting for ~85% of the PF* quenching events in PF-Ru, while electron transfer to produce a charge-separated state (i.e., ${}^1\text{PF}^* + \text{Ru}^{2+} \rightarrow \text{PF}^+ + \text{Ru}^{1+}$) takes place on a slower time scale, $\tau = 1.5$ ps. In PF-Ru, the apparent blue shift of the stimulated emission is due to the formation of PF⁺.

Assemblies incorporating PT, as well as scaffolds with mixed thiophene and fluorene content, PFT and PF2T (Figure 1), also show competitive energy and electron transfer. Like PF-Ru, all of these assemblies exhibit negative-going stimulated emission features that are quenched in the presence of the pendant Ru(II) complexes. Analysis of the quenching kinetics reveals that the electron transfer time across this series of polymers is relatively constant, varying between 1 and 2 ps (Figure 6).^{20–22} The energy transfer times, on the other hand, increase with greater thiophene content, and as a result, the

fraction of polymer excited states that decay through the energy transfer pathway also decreases across the series (Table 1).

Table 1. Energy and Electron Transfer Data for π -Conjugated Polymer Assemblies with Pendant Ru(II) Chromophores

assembly	energy transfer/ electron transfer ratio	energy transfer		electron transfer		λ (eV)
		τ (ps)	τ_{RET} (ps)	τ (ps)	$-\Delta G^\circ$ (eV)	
PF-Ru	85:15	0.45	0.45	1.5	0.72	↑
PFT-Ru	75:25	0.7	1.2	2.0	0.45	0.50–0.75
PF2T-Ru	25:75	4.8	4.0	1.8	0.46	
PT-Ru	15:85	8.1	10.0	1.1	0.50	↓

The trend in energy transfer rates across the polymer series can be understood in terms of the absorption and emission properties of assemblies. The rate constant for resonant energy transfer (RET) between a donor (D) and acceptor (A) separated by a distance R is given by

$$\frac{1}{\tau_{\text{RET}}} = \frac{1}{\tau_{\text{D}}} \left(\frac{R_0}{R} \right)^6 \quad (1)$$

where τ_{D} is the excited-state lifetime of the donor and R_0 is the Förster distance, the distance at which energy transfer is 50% efficient. The Förster distance can be estimated from independent spectroscopic measurements of the donor and acceptor according to

$$R_0^6 = A\Phi_{\text{D}}\kappa^2 \int_0^\infty F_{\text{D}}(\lambda)E_{\text{A}}(\lambda)\lambda^4 d\lambda \quad (2)$$

where Φ_{D} is the quantum yield of the donor in the absence of the acceptor and κ is a factor describing the relative orientations

of the donor and acceptor. The constant A is given by $A = 9000(\ln 10)/(128\pi^5 n^4 N_{\text{A}})$, where n is the refractive index and N_{A} is Avogadro's number. The integral in eq 2 describes the product of the emission spectrum of the donor normalized to unity area and the absorption spectrum of the acceptor, as illustrated in Figure 6.

The large energy transfer rate constant observed in the PF-Ru assembly results from the significant spectral overlap between the PF emission and the Ru absorption (Figure 6) and large quantum yield of PF*. The decrease in the energy transfer rate across the series is attributed to a systematic shift in the emission spectrum to lower energy with increasing thiophene content, which results in an overall decrease in the overlap between the donor emission and acceptor absorption, as well as a decrease in the quantum yield of the polymer (Φ_{D}). Energy transfer rates predicted using eq 1 are in good agreement with the experimentally observed values (Table 1).^{20–22}

The lifetime of the charge-separated state produced by electron transfer also depends upon the polymer backbone. While the charge-separated state in PF-Ru undergoes recombination (i.e., back electron transfer) to reform the ground state with $\tau = 6$ ns, in PT-Ru, it decays with $\tau \approx 20 \mu\text{s}$. The dramatic difference between these two assemblies may be a consequence of the high hole mobility of the PT polymer backbone,⁴⁰ which could quickly and efficiently separate the electron and the hole.

MULTIFUNCTIONAL BEHAVIOR

The eventual utilization of molecular assemblies in artificial photosynthetic applications will require that they perform multiple functions, including light harvesting and charge separation, as well as storage and transport of redox equivalents to catalytic sites. Multifunctional behavior is observed in the excited-state photophysics of PF-Ru assemblies anchored to TiO_2 through carboxylate groups placed on ~30% of the Ru

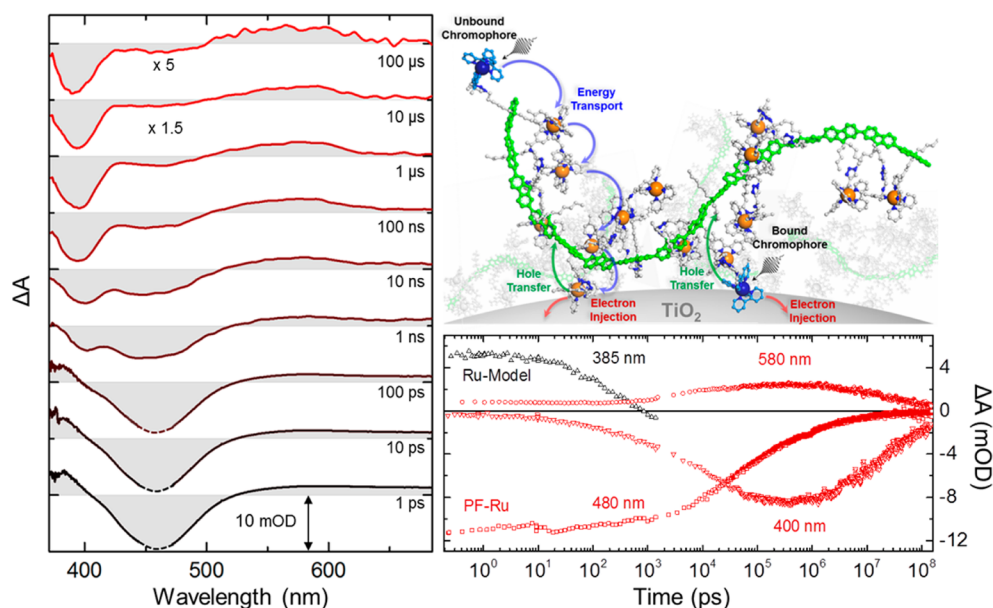


Figure 7. (left) Transient absorption difference spectra of a PF-Ru-loaded TiO_2 film following excitation at 450 nm from 1 ps to 100 μs . The 10 and 100 μs spectra have been scaled for clarity, while regions containing scatter from the 450 nm pump have been marked with a dashed line. (upper right) Illustration of the initial dynamic processes occurring following the excitation of the Ru(II) pendants within the PF-Ru assembly attached to the surface of a TiO_2 nanoparticle. (lower right) Combined kinetics traces from 200 fs to 150 μs for the PF-Ru assembly (red) at 400, 480, and 580 nm and the Ru-model (black) at 385 nm.

complexes.⁴¹ The result is a composite structure, in which the assembly is attached to the surface through a few complexes while the remaining chromophores serve as antennas for light absorption and excited-state transport.

The photophysics of this assembly on TiO₂ were studied across 9 decades of time using transient absorption spectroscopy. Photoexcitation of surface-bound Ru(II) sites results in prompt electron injection into the TiO₂, producing a Ru(III) species. The electron injection process is observed by monitoring the loss of the bipyridine radical anion (bpy^{•-}) absorption at 385 nm (Figure 7). Experiments performed on a model Ru complex that has the same ligand configuration as the pendant complexes in the PF-Ru assembly, but without the polymer backbone, show that the injection process is characterized by both fast ($\tau_1 = 60$ ps) and slow ($\tau_2 = 500$ ps) components.⁴² Following electron injection, the hole on the Ru(III) complex is transferred to the PF backbone, giving rise to the PF⁺ features at 400 and 580 nm that first appear at about 100 ps (Figure 7). The appearance of these features coincides with the loss of the Ru* due to electron injection, implying that hole transfer is fast ($\tau < 100$ ps) compared with the slower injection components. These PF⁺ features continue to grow in amplitude, reaching their peak at ~500 ns (Figure 7). This continued growth is attributed to photoexcitation of unbound complexes, which is followed by site-to-site energy transport of the excited state to the surface, electron injection, and transfer of the hole to the polymer (Figure 7). Charge recombination occurs between electrons within the TiO₂ and holes residing on the PF backbone. Monitoring the loss of the PF⁺ features indicates that the recombination time is greatly extended, with the charge-separated state persisting for up to 150 μ s. The formation of a long-lived charge-separated state is a desirable property for the production of solar fuels as it enables effective transfer of redox equivalents to be used in multielectron catalytic reactions.

SUMMARY AND CONCLUSIONS

The rational design of molecular assemblies for solar energy conversion will require a full understanding of the dynamical processes that occur following the absorption of light. The development of this detailed microscopic picture of the underlying energy and electron transfer events faces several challenges. Because of the structural complexity, the observed kinetics cannot be described by a single rate constant but reflect a superposition of many different processes that may include fundamental energy and electron transfer events, as well as conformational motions. Disentangling these contributions, which can span time scales ranging from femtoseconds to hundreds of microseconds, requires modeling that can link the observed kinetics to the underlying structure. Our work thus far has demonstrated that this is possible in systems exhibiting multiple functions, including light harvesting, charge separation, and storage. The lessons learned are being used in the design of the next generation of assemblies that will integrate catalytic sites for solar fuels production.

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Notes

The authors declare no competing financial interest.

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Gyu Leem received his B.S. in chemical engineering from the Hanyang University and Ph.D. in Chemistry from the University of Houston in 2008. In 2009, he moved to LG Chem and worked in the division of petrochemical and polymer before joining the University of Florida with Professor Kirk Schanze as a Postdoctoral Associate in 2012. His research focuses on designing and synthesizing polymer-based metal chromophores for potential use in light-harvesting antennas.

Alexander T. Gilligan is currently completing his B.S. in Chemistry at the UNC—Chapel Hill. As a member of the Papanikolas group, he has performed molecular dynamics simulations on polymer assemblies.

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REFERENCES

- (1) Alstrum-Acevedo, J. H.; Brennaman, M. K.; Meyer, T. J. Chemical Approaches to Artificial Photosynthesis. 2. *Inorg. Chem.* **2005**, *44*, 6802–6827.
- (2) Gust, D.; Moore, T. A.; Moore, A. L. Mimicking Photosynthetic Solar Energy Transduction. *Acc. Chem. Res.* **2001**, *34*, 40–48.
- (3) Sykora, M.; Maxwell, K. A.; DeSimone, J. M.; Meyer, T. J. Mimicking the Antenna-Electron Transfer Properties of Photosynthesis. *Proc. Natl. Acad. Sci. U.S.A.* **2000**, *97*, 7687–7691.
- (4) Fleming, C. N.; Maxwell, K. A.; DeSimone, J. M.; Meyer, T. J.; Papanikolas, J. M. Ultrafast Excited-State Energy Migration Dynamics in an Efficient Light-Harvesting Antenna Polymer Based on Ru(II) and Os(II) Polypyridyl Complexes. *J. Am. Chem. Soc.* **2001**, *123*, 10336–10347.
- (5) Fang, Z.; Ito, A.; Stuartt, A. C.; Luo, H. L.; Chen, Z. F.; Vinodgopal, K.; You, W.; Meyer, T. J.; Taylor, D. K. Soluble Reduced Graphene Oxide Sheets Grafted with Polypyridylruthenium-Derivatized Polystyrene Brushes as Light Harvesting Antenna for Photovoltaic Applications. *ACS Nano* **2013**, *7*, 7992–8002.
- (6) Devadoss, C.; Bharathi, P.; Moore, J. S. Energy Transfer in Dendritic Macromolecules: Molecular Size Effects and the Role of an Energy Gradient. *J. Am. Chem. Soc.* **1996**, *118*, 9635–9644.
- (7) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. Designing Dendrimers Based on Transition Metal Complexes. Light-Harvesting Properties and Predetermined Redox Patterns. *Acc. Chem. Res.* **1998**, *31*, 26–34.
- (8) Nantalaksakul, A.; Reddy, D. R.; Bardeen, C. J.; Thayumanavan, S. Light Harvesting Dendrimers. *Photosynth. Res.* **2006**, *87*, 133–150.
- (9) McCafferty, D. G.; Friesen, D. A.; Danielson, E.; Wall, C. G.; Saderholm, M. J.; Erickson, B. W.; Meyer, T. J. Photochemical Energy Conversion in a Helical Oligoproline Assembly. *Proc. Natl. Acad. Sci. U.S.A.* **1996**, *93*, 8200–8204.
- (10) Knorr, A.; Galoppini, E.; Fox, M. A. Photoinduced Intramolecular Electron Transfer in Dichrophore-appended Alpha-helical Peptides: Spectroscopic Properties and Preferred Conformations. *J. Phys. Org. Chem.* **1997**, *10*, 484–498.
- (11) Serron, S. A.; Aldridge, W. S.; Fleming, C. N.; Danell, R. M.; Baik, M. H.; Sykora, M.; Dattelbaum, D. M.; Meyer, T. J. Evidence for Through-Space Electron Transfer in the Distance Dependence of Normal and Inverted Electron Transfer in Oligoproline Arrays. *J. Am. Chem. Soc.* **2004**, *126*, 14506–14514.
- (12) Wilger, D. J.; Bettis, S. E.; Materese, C. K.; Minakova, M.; Papoian, G. A.; Papanikolas, J. M.; Waters, M. L. Tunable Energy Transfer Rates via Control of Primary, Secondary, and Tertiary Structure of a Coiled Coil Peptide Scaffold. *Inorg. Chem.* **2012**, *51*, 11324–11338.
- (13) Bettis, S. E.; Ryan, D. M.; Gish, M. K.; Alibabaei, L.; Meyer, T. J.; Waters, M. L.; Papanikolas, J. M. Photophysical Characterization of a Helical Peptide Chromophore–Water Oxidation Catalyst Assembly on a Semiconductor Surface Using Ultrafast Spectroscopy. *J. Phys. Chem. C* **2014**, *118*, 6029–6037.
- (14) Davis, W. B.; Ratner, M. A.; Wasielewski, M. R. Conformational Gating of Long Distance Electron Transfer through Wire-like Bridges in Donor-Bridge-Acceptor Molecules. *J. Am. Chem. Soc.* **2001**, *123*, 7877–7886.
- (15) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. Contemporary Issues in Electron Transfer Research. *J. Phys. Chem.* **1996**, *100*, 13148–13168.
- (16) Fleming, C. N.; Dupray, L. M.; Papanikolas, J. M.; Meyer, T. J. Energy Transfer between Ru(II) and Os(II) Polypyridyl Complexes Linked to Polystyrene. *J. Phys. Chem. A* **2002**, *106*, 2328–2334.
- (17) Fleming, C. N.; Jang, P.; Meyer, T. J.; Papanikolas, J. M. Energy Migration Dynamics in a Ru(II)- and Os(II)-Based Antenna Polymer Embedded in a Disordered, Rigid Medium. *J. Phys. Chem. B* **2004**, *108*, 2205–2209.
- (18) Fleming, C. N.; Brennaman, M. K.; Papanikolas, J. M.; Meyer, T. J. Efficient, Long-range Energy Migration in Ru-II Polypyridyl Derivatized Polystyrenes in Rigid Media. Antennae for Artificial Photosynthesis. *Dalton Trans.* **2009**, 3903–3910.
- (19) Shaw, G. B.; Papanikolas, J. M. Triplet-triplet Annihilation of Excited States of Polypyridyl Ru(II) Complexes Bound to Polystyrene. *J. Phys. Chem. B* **2002**, *106*, 6156–6162.
- (20) Wang, L.; Puodziukynaite, E.; Vary, R. P.; Grumstrup, E. M.; Walczak, R. M.; Zolotarskaya, O. Y.; Schanze, K. S.; Reynolds, J. R.; Papanikolas, J. M. Competition between Ultrafast Energy Flow and Electron Transfer in a Ru(II)-Loaded Polyfluorene Light-Harvesting Polymer. *J. Phys. Chem. Lett.* **2012**, *3*, 2453–2457.
- (21) Wang, L.; Puodziukynaite, E.; Grumstrup, E. M.; Brown, A. C.; Keinan, S.; Schanze, K. S.; Reynolds, J. R.; Papanikolas, J. M. Ultrafast Formation of a Long-Lived Charge-Separated State in a Ru-Loaded Poly(3-hexylthiophene) Light-Harvesting Polymer. *J. Phys. Chem. Lett.* **2013**, *4*, 2269–2273.
- (22) Puodziukynaite, E.; Wang, L.; Schanze, K. S.; Papanikolas, J. M.; Reynolds, J. R. Poly(fluorene-co-thiophene)-based Ionic Transition-Metal Complex Polymers for Solar Energy Harvesting and Storage Applications. *Polym. Chem.* **2014**, *5*, 2363–2369.
- (23) McCusker, J. K. Femtosecond Absorption Spectroscopy of Transition Metal Charge-transfer Complexes. *Acc. Chem. Res.* **2003**, *36*, 876–887.
- (24) Gillespie, D. T. Exact Stochastic Simulation of Coupled Chemical-reactions. *J. Phys. Chem.* **1977**, *81*, 2340–2361.
- (25) Chen, Z.; Grumstrup, E. M.; Gilligan, A. T.; Papanikolas, J. M.; Schanze, K. S. Light-Harvesting Polymers: Ultrafast Energy Transfer in Polystyrene-based Arrays of π -Conjugated Chromophores. *J. Phys. Chem. B* **2014**, *118*, 372–378.
- (26) Yeow, E. K. L.; Ghigino, K. P.; Reek, J. N. H.; Crossley, M. J.; Bosman, A. W.; Schenning, A. P. H. J.; Meijer, E. W. The Dynamics of Electronic Energy Transfer in Novel Multiporphyrin Functionalized Dendrimers: A Time-Resolved Fluorescence Anisotropy. *J. Phys. Chem. B* **2000**, *104*, 2596–2606.
- (27) Kleiman, V. D.; Melinger, J. S.; McMorrow, D. Ultrafast Dynamics of Electronic Excitations in a Light-Harvesting Phenylacetylene Dendrimer. *J. Phys. Chem. B* **2001**, *105*, 5595–5598.
- (28) Akselrod, G. M.; Deotare, P. B.; Thompson, N. J.; Lee, J.; Tisdale, W. A.; Baldo, M. A.; Menon, V. M.; Bulovic, V. Visualization of Exciton Transport in Ordered and Disordered Molecular Solids. *Nat. Commun.* **2014**, *5*, No. 3646.
- (29) Bredas, J. L.; Beljonne, D.; Coropceanu, V.; Cornil, J. Charge-Transfer and Energy-Transfer Processes in π -Conjugated Oligomers and Polymers: A Molecular Picture. *Chem. Rev.* **2004**, *104*, 4971–5003.
- (30) Banerji, N.; Cowan, S.; Vauthey, E.; Heeger, A. J. Ultrafast Relaxation of the Poly(3-hexylthiophene) Emission Spectrum. *J. Phys. Chem. C* **2011**, *115*, 9726–9739.
- (31) Hintschich, S. I.; Dias, F. B.; Monkman, A. P. Dynamics of Conformational Relaxation in Photoexcited Oligofluorenes and Polyfluorene. *Phys. Rev. B* **2006**, *74*, No. 045210.
- (32) Nelson, T.; Fernandez-Alberti, S.; Roitberg, A. E.; Tretiak, S. Nonadiabatic Excited-state Molecular Dynamics: Modeling Photo-physics in Organic Conjugated Materials. *Acc. Chem. Res.* **2014**, *47*, 1155–1164.
- (33) Hwang, I.; Scholes, G. D. Electronic Energy Transfer and Quantum-Coherence in π -Conjugated Polymers. *Chem. Mater.* **2011**, *23*, 610–620.

(34) Bredas, J. L.; Heeger, A. J. Theoretical Investigation of Gas-Phase Torsion Potentials Along Conjugated Polymer Backbones - Polyacetylene, Polydiacetylene, and Polythiophene. *Macromolecules* **1990**, *23*, 1150–1156.

(35) Chen, H. L.; Huang, Y. F.; Lim, T. S.; Su, C. H.; Chen, P. H.; Su, A. C.; Wong, K. T.; Chao, T. C.; Chan, S. L.; Fann, W. Excited-State Backbone Twisting of Polyfluorene as Detected from Photo-thermal After-Effects. *J. Phys. Chem. B* **2009**, *113*, 8527–8531.

(36) Wells, N. P.; Blank, D. A. Correlated Exciton Relaxation in Poly(3-hexylthiophene). *Phys. Rev. Lett.* **2008**, *100*, No. 086403.

(37) Busby, E.; Carroll, E. C.; Chinn, E. M.; Chang, L. L.; Moule, A. J.; Larsen, D. S. Excited-State Self-Trapping and Ground-State Relaxation Dynamics in Poly(3-hexylthiophene) Resolved with Broadband Pump-Dump-Probe Spectroscopy. *J. Phys. Chem. Lett.* **2011**, *2*, 2764–2769.

(38) Westenhoff, S.; Beenken, W. J. D.; Friend, R. H.; Greenham, N. C.; Yartsev, A.; Sundstrom, V. Anomalous Energy Transfer Dynamics Due to Torsional Relaxation in a Conjugated Polymer. *Phys. Rev. Lett.* **2006**, *97*, No. 166804.

(39) Heimel, G.; Daghofer, M.; Gierschner, J.; List, E. J. W.; Grimsdale, A. C.; Mullen, K.; Beljonne, D.; Bredas, J. L.; Zojler, E. Breakdown of the Mirror Image Symmetry in the Optical Absorption/Emission Spectra of Oligo(para-phenylene)s. *J. Chem. Phys.* **2005**, *122*, 54501–54511.

(40) Sirringhaus, H.; Tessler, N.; Friend, R. H. Integrated Optoelectronic Devices Based on Conjugated Polymers. *Science* **1998**, *280*, 1741–1744.

(41) Leem, G.; Morseth, Z. A.; Puodziukynaite, E.; Jiang, J.; Zhen, F.; Gilligan, A. T.; Reynolds, J. R.; Papanikolas, J. M.; Schanze, K. S. Light-Harvesting and Charge-Separation in a π -Conjugated Antenna Polymer Bound to TiO₂. *J. Phys. Chem. C* **2014**, *118*, 28535–28541.

(42) It is interesting to note that this metal complex does not exhibit the sub-picosecond injection component that is commonly observed in dye-sensitized solar cells. Ongoing work in our laboratory suggests that its absence is the result of the ligand functionalization, which acts to lower the energy of the MLCT injecting state and slow injection.