Energy Transfer Dynamics in Re\textsuperscript{I}—Based Polynuclear Assemblies: A Quantitative Application of Förster Theory

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The synthesis, structure, and photophysical properties of a new family of tetranuclear FeRe\textsubscript{3} chromophore-quencher complexes having the general form [Fe(pyacac)]\textsubscript{3}(Re(bpy))(CO)\textsubscript{3}(OTf)\textsubscript{3} (where pyacac = 3-(4-pyridyl)-acetylacetonate and bpy\textsuperscript{−} is 4,4′,5,5′-tetramethyl-2,2′-bipyridine (tmb, 1), 2,2′-bipyridine (bpy, 2), and 4,4′-diethylester-2,2′-bipyridine (deeb, 3)) are reported. Time-resolved emission data acquired in room-temperature CH\textsubscript{2}Cl\textsubscript{2} solutions exhibited single exponential decay kinetics with observed lifetimes of 450 ± 30 ps, 755 ± 40 ps, and 2.5 ± 0.1 ns for complexes 1, 2, and 3, respectively. The emission in each case is assigned to the decay of the Re\textsuperscript{I}-based \textsuperscript{3}MLCT excited state; the lifetimes are all significantly less than the corresponding AlRe\textsubscript{3} analogues (2250 ± 100 ns, 560 ± 30 ns, and 235 ± 20 ns for 4, 5, and 6, respectively), which were also prepared and characterized. Electron transfer is found to be thermodynamically unfavorable for all three Re\textsuperscript{I}-containing systems: this fact coupled with the absence of optical signatures for the expected charge-separated photoproducts in the time-resolved differential absorption spectra and favorable spectral overlap between the donor emission and the acceptor absorption profiles implicates dipolar energy transfer from the Re\textsuperscript{I}-based excited state to the high-spin Fe\textsuperscript{III} core as the dominant quenching pathway in these compounds. Details obtained from the X-ray structural data of complex 2 allowed for a quantitative application of Förster energy transfer theory by systematically calculating the separation and spatial orientation of the donor and acceptor transition moment dipoles. Deviations between the calculated and observed rate constants for energy transfer were less that a factor of 3 for all three complexes. This uncommonly high degree of precision testifies to both the appropriateness of the Förster model as applied to these systems, as well as the accuracy that can be achieved in quantifying energy transfer rates if relative dipole orientations can be accounted for explicitly.

Introduction

Elucidating the mechanism of excited-state reactivity is a necessary first step for understanding and ultimately manipulating complex photoinduced chemical processes.\textsuperscript{1–4} Accordingly, numerous fundamental studies of excited-state dynamics have been reported in the literature. Assemblies based on d\textsuperscript{6} polypyridyl complexes of Re\textsuperscript{I}, Ru\textsuperscript{II}, and Os\textsuperscript{II} have garnered particular attention because of the relative stability of their excited states, well documented ground and excited-state electronic properties, and the ability one has to tune these properties through synthetic means. Both electron and energy transfer processes have been the subject of intense scrutiny. As a result, much has been learned about the factors that govern both these types of excited-state reactions in transition-metal based systems.\textsuperscript{5–14}

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With regard to energy transfer, the two most important mechanisms are electron superexchange (Dexter)\(^1\) and dipole–dipole coupling ( Förster).\(^6\) Dexter energy transfer is subject to a distance dependence that falls off as \(\exp(-2r)\) due to its reliance on orbital overlap. As such, it is usually relegated to covalently linked systems in which the donor and acceptor are in close proximity (e.g., 5–10 Å or less).\(^7\)–\(^22\) Förster transfer is a through-space mechanism that occurs when the donor emission dipole nonradiatively couples to an absorptive dipole in the acceptor.\(^23\)–\(^25\) The dipolar nature of this interaction gives rise to a shallower \(r^{-6}\) dependence, allowing this mechanism to be operative over much longer distances. Förster-type reactivity is therefore usually dominant in systems that place the lowest energy donor and acceptor distances and \(\kappa\) is the refractive index of the solvent, \(N_A\) is Avogadro’s number, \(\tau_D\) is the excited-state lifetime of the donor, \(R\) is the donor–acceptor separation, and \(J\) is a spectral overlap integral that essentially quantifies the resonance condition necessary for dipole–dipole coupling. This latter term can be evaluated from the spectroscopic properties of the system according to eq 2,\(^{30}\)

\[
k_{E_J} = \frac{9000 \ln(10) \kappa^2 \Phi_D J}{128 \pi^4 \eta^4 N_A \tau_D R^6}
\]

where \(\kappa^2\) is the dipole orientation factor, \(\Phi_D\) is the radiative quantum yield of the donor, \(\eta\) is the refractive index of the solvent, \(N_A\) is Avogadro’s number, \(\tau_D\) is the excited-state lifetime of the donor, \(R\) is the donor–acceptor separation, and \(J\) is a spectral overlap integral that essentially quantifies the resonance condition necessary for dipole–dipole coupling. This latter term can be evaluated from the spectroscopic properties of the system according to eq 2.\(^{30}\)

\[
J = \int_0^{\infty} \frac{\tilde{R}_D(\nu) \tilde{R}_A(\nu)}{\nu^4} d\nu
\]

where \(\tilde{R}_D\) is the (normalized) emission spectrum of the donor and \(\tilde{R}_A\) is the absorption profile of the acceptor in units of molar absorptivity. The orientation factor \(\kappa^2\) defines the spatial relationship between the transition dipoles of the donor and acceptor. This is expressed mathematically in eq 3,

\[
\kappa^2 = (\cos \Theta_T - 3 \cos \Theta_D \cos \Theta_A)^2
\]

where \(\Theta_T\) is the angle between the transition dipole moments of the donor and the acceptor, and \(\Theta_D\) and \(\Theta_A\) are the angles these two transition dipoles make with a vector corresponding to their through-space connection.

Although eqs 1–3 constitute a complete description of the rate of dipolar energy transfer, quantifying the donor–acceptor distance (\(R\)) and the orientation factor (\(\kappa^2\)) can be quite difficult, particularly in polynucleon donor–acceptor assemblies.\(^{31}\)–\(^{40}\) Taking \(R\) as the metal–metal distance is a reasonable assumption when structural data are not available, but in the point-dipole approximation of Förster theory this may or may not accurately reflect the relevant distance in systems comprised of donor and acceptor states that are charge-transfer in nature. In addition, the orientation factor of \(\kappa^2 = \frac{2}{3}\) typically invoked represents an isotropic value for species sampling all possible angular distributions.\(^{41}\) While appropriate for bimolecular energy transfer processes, this approximation may not be reasonable given the rotational barriers that likely exist in covalently attached donor–acceptor complexes. The ambiguities that can arise with regard to these two variables often lead to a large variance between experiment and theory.

Recently, Moore et al. applied Förster theory in conjunction with molecular modeling calculations to study the energy transfer dynamics of naphthalene- and anthracene-appended Zn\(^{II}\) macrocycles.\(^{42}\)–\(^{43}\) These authors obtained excellent agreement between experiment and theory when employing quantitatively determined donor–acceptor distances and...
orientation factors for the various conformers identified through the modeling studies. We sought to take a similar approach in the context of an inorganic charge-transfer system. Herein, we report the synthesis, structure, and photophysical properties of a series of mixed-metal donor–acceptor assemblies: [Fe(pyacac)3(Re(tmb)(CO)3)3](OTf)2 (1), [Fe(pyacac)3(Re(bpy)(CO)3)3](OTf)2 (2), and [Fe(pyacac)3(Re(deeb)(CO)3)3](OTf)3 (3) (where pyacac = 3-(4-pyridyl)-acetylacetonate, tmb = 4,4’,5,5’-tetramethyl-2,2’-bipyridine, bpy = 2,2’-bipyridine, and deeb = 4,4’-diethylester-2,2’-bipyridine). These compounds provide a series of geometrically well-defined systems in which the donor and acceptor transition dipoles, and hence the orientation factor $\kappa^2$, can be explicitly determined. Moreover, variations in the emission energy afforded by the different bipyridyl ligands attached to the ReI metal center provides for systematic modulation of the donor–acceptor spectral overlap. Our results demonstrate the level of agreement one can achieve between experiment and theory for this class of compounds when all of the variables involved in eq 1 are explicitly taken into account.

**Experimental Section**

**General Information.** All solvents used were purified and dried according to previously reported methods. Spectroscopic grade CH2Cl2 was used for all photophysical measurements; the solvent was dried under CaH2 reflux until no water was detected by 1H NMR and degassed using freeze–pump–thaw techniques. 3-(4-pyridyl)-2,4-pentanedione was purchased from TCI America. Elemental analyses and FT-IR data were obtained following literature procedures. 3-phenyl-2,4-pentanedione was obtained analogous to Fe(pyacac)3. Yield: 238 mg (78%).

**Tris(3-phenyl-acetylacetonato)iron(III), Fe(pyacac)3.** This compound was prepared analogous to Fe(pyacac)3. An amount of 230 mg (0.360 mmol) of Re(tmb)(CO)3(OTf) was dissolved in 75 mL of hot THF, after which 70 mg (0.12 mmol) of Fe(pyacac)3 was added and the solution purged with argon for 20 min. The reaction mixture was fit with a condenser and stirred under argon for 3 days in hot THF in the dark, during which time a red solution formed along with an orange precipitate. The precipitate was collected and the filtrate was concentrated under vacuum to yield additional orange solid. The combined precipitates were dissolved in CH2Cl2, filtered through celite, and the solvent removed under vacuum. The product was recrystallized several times from CH3Cl/pentane (1:1 v/v). Yield: 155 mg (52%).

**[Fe(pyacac)3(Re(tmb)(CO)3)3](OTf)3 (1).** In 25 mL of THF, 70 mg (0.12 mmol) of [Fe(pyacac)3](OTf)3 was dissolved, and 210 mg (0.365 mmol) of Re(tmb)(CO)3(OTf) was added. The solution was flushed with argon for 20 min then stirred in the dark for 3 days at room temperature. An orange solid that precipitated out of solution was collected and washed with hexanes. The solid was dissolved in CH2CN, filtered through celite, and the solvent removed under vacuum. The product was recrystallized several times from acetonitrile/ether (1:1 v/v).

**[Fe(pyacac)3(Re(bpy)(CO)3)3](OTf)2 (2).** In 25 mL of THF, 70 mg (0.12 mmol) of [Fe(pyacac)3](OTf)3 was dissolved, and 210 mg (0.365 mmol) of Re(bpy)(CO)3(OTf)2 was added. The solution was flushed with argon for 20 min then stirred in the dark for 3 days at room temperature. An orange solid that precipitated out of solution was collected and washed with hexanes. The solid was dissolved in CH2CN, filtered through celite, and the solvent removed under vacuum. The product was recrystallized several times from acetonitrile/ether (1:1 v/v).

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analyses and data were integrated with the program SAINT. The Cryosystems low temperature device. Crystallographic data are 0.71073Å. Data were collected at 20°C using graphite-monochromatic Mo Kα radiation (λ = 0.71073Å). The structure determinations may be found in Supporting Information.


Table 1. Crystallographic Data for [Fe(pyacac)(Re(bpy)(CO)3)3](OTf)3 (2) and [Al(pyacac)(Re(bpy)(CO)3)3](OTf)3 (5)

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<tr>
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<td>C72H54N9F9O24S3AlRe3</td>
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<td>2282.00</td>
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<td>a/Å</td>
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<tr>
<td>b/Å</td>
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<td>GOF</td>
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Table 2. Selected Bond Distances (Å) and Angles (deg) for [Fe(pyacac)(Re(bpy)(CO)3)3](OTf)3 (2) and [Al(pyacac)(Re(bpy)(CO)3)3](OTf)3 (5)

<table>
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<td>Fe(1)–O(1)</td>
<td>1.992(6)</td>
<td>1.877(10)</td>
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<td>1.970(7)</td>
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<tr>
<td>Fe(1)–O(6)</td>
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<td>1.871(11)</td>
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<td>1.894(11)</td>
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<td>2.218(7)</td>
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<td>Re(3)–N(7)</td>
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<td>Fe(1)–Re(1)</td>
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<td>2.974(10)</td>
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<tr>
<td>Fe(1)–Re(3)</td>
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<td>3.000(6)</td>
</tr>
<tr>
<td>Bond Angles (deg)</td>
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<td>5</td>
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<td>C(23)–Re(1)–N(1)</td>
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<td>93.0(6)</td>
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Anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were localized in their calculation positions and refined by using theriding model. Further details concerning the structure determinations may be found in Supporting Information.

Electrochemistry. Electrochemical measurements were carried out in a N2-filled drybox (Vacuum Atmospheres) using a BAS CV-50W electrochemical analyzer. A standard three-electrode arrangement was utilized consisting of Pt working and counter electrodes and an Ag/AgNO3 reference electrode. Measurements were carried out in either CH2Cl2 or CH3CN solutions containing 0.1 M NBu4PF6. The choice of solvent was dictated by the potential window required to observe a given redox couple; in cases where

Table 3. Formulations

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<tr>
<th>Formula</th>
<th>Crystal Structure</th>
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<tr>
<td>C27H54N9O20F9S3AlRe3</td>
<td>triclinic</td>
<td>2310.87, 2282.00</td>
</tr>
<tr>
<td>C72H54N9F9O24S3AlRe3</td>
<td>triclinic</td>
<td>611.6 (100)</td>
</tr>
</tbody>
</table>

Knight et al.

a compound could be examined in both solvents, differences in the observed potentials were found to be minor. Data were acquired using both cyclic and differential pulse voltammetry; the scan rate for the CV measurements was 100 mVs. Values of the midpoint potentials obtained by the two techniques were comparable for the reversible Fe- and ligand-based reductions, whereas slightly larger differences were noted for the quasi-reversible Re-based oxidations. The potentials reported in Table 3 are based on the cyclic voltammetry measurements and are quoted relative to the ferrocene/ferrocnium couple which was used as an internal standard.

Electronic Absorption and Steady-State Emission Spectroscopies. Extinction coefficients for all compounds were acquired in CH₂Cl₂ solutions using a Hewlett-Packard 8452A diode array spectrophotometer. Steady-state emission spectra were acquired using a Spex Fluoromax fluorimeter and corrected for instrumental response using a NIST standard of spectral irradiance (Optronic Laboratories, Inc., OL220 M tungsten quartz lamp). Spectra were acquired on samples dissolved in thoroughly degassed CH₂Cl₂ under optically dilute conditions (o.d. ∼ 0.1) and sealed under an argon atmosphere in 1 cm path length quartz cuvettes.

Radiative quantum yields (Φᵣ) were determined relative to fac-[Re(bpy)(CO)₃(4-Etpy)][PF₆] (Φᵣ = 0.18 in CH₂Cl₂). Quantum yields were calculated according to eq 4,

\[ \Phi_{\text{unk}} = \frac{I_{\text{unk}}}{I_{\text{std}}} \left( \frac{\eta_{\text{unk}}}{\eta_{\text{std}}} \right)^2 \]

where Φᵣ and Φᵣ are the radiative quantum yields of the sample and the standard, respectively, Iᵣ and Iᵣ represent the areas of the corrected emission profiles for the sample and the standard, Aᵣ and Aᵣ are the absorbance values of the sample and the standard at the excitation wavelength, and ηᵣ and ηᵣ correspond to the indices of refraction of the sample and standard solutions (taken to be equal to the neat solvents). Excitation wavelengths were 355 nm for the bpy and tmh analogues and 400 nm for the deeb analogues. The corrected excitation spectrum of fac-[Re(bpy)(CO)₃(4-Etpy)][PF₆] in CH₂Cl₂ overlaid well with the compound’s absorption spectrum over the range of wavelengths examined (355–400 nm), implying that the radiative quantum yield for fac-[Re(bpy)(CO)₃(4-Etpy)][PF₆] does not vary significantly over this spectral window. The reported value of Φᵣ = 0.18 was therefore used for determining the radiative quantum yields at both λₘ = 355 and 400 nm.

Radiative quantum yields are not being reported for complexes 1–3 because of the presence of an emissive impurity. The source of the impurity was traced to a small amount of dissociated complex present in solution, most likely generated by water in the CH₂Cl₂ solvent. Despite our best efforts at drying the CH₂Cl₂, there was an unacceptably large variance in repeated measurements of Φᵣ. Because of the difference in time scales associated with excited-state decay between those emissive fragments and the intact assembly, the presence of these impurities does not significantly affect the kinetic analyses of these systems.

Values for the zero-point energy gap (E₀) of the Re¹⁺-based ³MLCT excited states were determined by fitting the emission profiles of complexes 4–6 based on the approach described by Claude and Meyer. Wavelength data were converted to energy units following the correction of Parker and Rees; the best fit was determined by visual inspection of the results of a least-squares minimization routine.

Time-Resolved Emission Spectroscopy. Nanosecond time-resolved emission data for the AlRe₃ model complexes 1–6 were collected using a Nd:YAG-based laser spectrometer that has been described previously. Data were acquired at room temperature in thoroughly degassed CH₂Cl₂ solutions having absorbances of ∼0.1 at the excitation wavelength (λₑx = 355 nm for complexes 4 and 5 and 420 nm for complex 6). Samples were sealed under an argon atmosphere in 1 cm path length quartz cuvettes. The decay traces correspond to an average of 250 shots of the signal probed at the emission maximum of each compound.

Pico-second time-resolved emission data for the FeRe₃ complexes 1–3 were collected using a time-correlated single photon counting (TSCPC) apparatus that has been described previously. Data were acquired in thoroughly degassed CH₂Cl₂ solutions having absorbances of ∼0.1 at the excitation wavelength (λₑx = 370 nm for complexes 1 and 2 and 430 nm for complex 3). Samples were sealed under an argon atmosphere in 1 cm path length quartz cuvettes. Each reported decay trace corresponds to a signal average of six data sets, with each data set resulting from about 1 h of data acquisition time. The decay traces for all three complexes manifest a small baseline offset within the data acquisition window because of the presence of the impurity mentioned above; this was incorporated into the kinetic model. Data were fit using the OriginPro 7.5 software package.

Time-resolved Absorption Spectroscopy. Nanosecond time-resolved absorption measurements were collected using a Nd:YAG-based laser spectrometer that has been described previously. Data were acquired on thoroughly degassed CH₂Cl₂ solutions in 1 cm path length sealed quartz cuvettes. Sample absorbance was ∼0.6 at the excitation wavelength of 355 nm. Excitation energies at the sample were about 2 mJ per pulse; all data were checked for linearity with respect to pump power, and steady-state absorption spectra were acquired before and after data acquisition to ensure...
the integrity of the sample. Differential absorption spectra were
generated by plotting the amplitudes of fits of the decay kinetics
acquired as a function of probe wavelength.

Subnanosecond time-resolved data were obtained for complex
1 using a femtosecond time-resolved absorption spectrometer that
is described elsewhere.52b Samples were dissolved in CH2Cl2 in
an Ar atmosphere drybox and placed in 1 mm path length quartz
cuvettes with absorbance values of \( \sim 0.6 \) at the excitation wave-
length \( \lambda_{\text{exc}} = 370 \text{ nm} \). Single-wavelength kinetics data were
collected at \( \lambda_{\text{obs}} = 700 \text{ nm} \) following \( \sim 100 \text{ fs} \) excitation at 370
nm with a pump power of about 4 \( \mu \text{J} \). Single-photon excitation
was confirmed by the linearity of the signal response with respect
to pump power. Acquisition of full spectra for complex 1 was
hampered by the formation of a photoprotein that precipitated over
the course of several hours of data acquisition. Nevertheless, the
data were sufficient to establish that identical kinetics are observed
across the entire visible probe window; this will be elaborated upon
in the Results and Discussion section. All data were fit using
programs of local origin.

Fürster Energy Transfer Rate Calculations. Calculations of
energy transfer rates were carried out based on eqs 1–3. Donor–acceptor distances and angles were measured using the
single-crystal X-ray structure data of complex 2 with the Diamond
3.1d crystal structure and visualization software.57

Results and Discussion

Synthesis and Characterization. Our interest in these
systems was to investigate energy and/or electron transfer
processes in structurally well-defined polynuclear charge-
transfer assemblies. The choice of using ReI and FeIII was
based on the well-known MLCT-based reactivity of ReI and
the propensity for FeIII to act as both an energy and electron acceptor.58–65 The utilization of the M(pyacac)3 core (M =
FeIII and AlIII) as a ligand for Re(bpy)(CO)3(OTf) allowed the pyridyl group to displace the weakly coordinating triflate
anion and generate the tricationic FeRe3 and AlRe3 complexes.
The formation of the tetranuclear assemblies was facilitated by the low steric crowding afforded by the roughly
120° separation of the three pyacac ligands.

The ESI-MS data for complexes 1–6 in acetonitrile
solution are consistent with the formation of the desired
FeRe3 and AlRe3 assemblies. For example, complex 2 shows
peaks corresponding to \{[Fe(pyacac)3(Re(bpy)(CO)3)3] \}1+,
\{[Fe(pyacac)3(Re(bpy)(CO)3)3](OTf) \}2+,
and \{[Fe(pyacac)3-
(Re(bpy)(CO)3)3](OTf) \}4+. X-ray quality crystals for complexes
2 and 5 were generated by diffusion of ether into an
acetonitrile solution of the complexes over the course of
approximately 1 week; this in turn provides additional
evidence for the general robustness of complexes 1–6 in
solution. Nevertheless, the FeIII-containing complexes 1–3
were found to be susceptible to slight decomposition in the
presence of water. As mentioned in the Experimental Section,
this was established via single-photon counting emission
spectroscopy through the detection of a highly emissive,
long-lived excited-state species. Because FeIII compounds are
nonemissive, this impurity is most likely a Re-bpy’-containing
fragment resulting from displacement of the pyacac ligand by adventitious H2O. This decomposition pathway is
not too surprising given the lability of high-spin FeIII48 and its
propensity to bind H2O, but the extremely low intensity of the
TCSPC signal corresponding to this species indicates that this
represents a very minor component in solution.

The \( \tau \) values for complexes 1–6 in acetonitrile are
consistent with high-spin FeIII and compare favorably with
other structurally characterized examples of FeIII-acac sys-
tems.48 Significantly shorter metal–oxygen bonds (ca. 0.1
Å) are observed for complex 5: such differences are to be
expected given the smaller ionic radius of AlIII.48 The
structures of the Re(bpy)(CO)3 moieties in both molecules are
unremarkable, exhibiting the pseudo-C3v coordination common to ReI complexes in this class.66–69 Not surprisingly, the metric details of the ReI fragment are
insensitive to the identity of the central metal ion: bond
distances, and angles associated with the primary coordina-
tion sphere as well as within the bipyridyl ligand itself are
identical within experimental error for the FeIII and AlIII
complexes. Slight differences are noted in the ReI•••MII
distances, with complex 5 being uniformly shorter by \( \sim0.1\text{ Å} \).

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Bonn, Germany, 2006.
1976, 98, 6536.
604.
Soc. 2004, 126, 6710.
mainly because of the decrease in metal–oxygen bond lengths relative to complex 2. Despite these minor differences, there is considerable structural homology between the two complexes, underscoring the appropriateness of using AlIII as a structurally and electronically benign replacement for FeIII in this system. Our efforts to obtain X-ray quality crystals for complexes 1, 3, 4, and 6 have thus far been unsuccessful; however, we do not expect that substituent changes on the periphery of the bipyridyl ligand will have any significant effect on the basic structural features of this system.

**Electrochemistry.** The electrochemical properties of complexes 1–6 were examined using both cyclic and differential pulse voltammetry; the data are given in Table 3. The availability of the AlIII model complexes greatly simplifies assigning the features observed for all six complexes because of the redox-inert nature of this ion. Accordingly, the single reduction waves seen for complexes 4–6 can be immediately ascribed to the bipyridyl ligand of the Re moiety in each case. The positive shift in potential across the series is consistent with the more electron withdrawing nature of the substituents as one progresses from the methyls of tmb (4) to the diethylester groups in complex 6. Similarly, the oxidation waves seen for all three complexes are easily assigned to the ReI/ReII couple. The influence of the bipyridyl substituents are apparent in these data as well, with the more electron deficient ligand giving rise to the most positive oxidation potential for the Re center. The results are all consistent with what has been observed for complexes of the general form fac-[Re(4,4″-X2-bpy)(CO)3(4-Etpy)](PF6) previously reported in the literature.

Given these assignments, the reductions at ca. −0.9 V observed for complexes 1–3 are clearly associated with the FeIII center. It can be seen that modification of the bipyridyl ligand has no discernible influence on the redox properties of the central Fe ion. In a similar vein, we note that the ligand reduction and ReI oxidation potentials of all three Fe-containing compounds are essentially identical to what was observed for the AlIII analogs. These data are indicative of (relatively) weak electronic coupling between the central metal ion and the peripheral chromophores.

**Electronic Absorption Spectroscopy.** The electronic absorption spectra of complexes 1–6 have been acquired in room-temperature CH2Cl2 solutions. Spectra for complexes 3 and 6 are shown in Figure 2; all six spectral profiles can be found in Supporting Information, Figure S1. ReI poly(pyridyl) complexes are typically characterized by a1A1 f1MLCT absorption that falls in the range of approximately 330 to 430 nm with the energy of the transition generally

Figure 1. Drawing of the cations of [Fe(pyacac)3(Re(bpy)(CO)3)3](OTf)3 (2, left) and [Al(pyacac)3(Re(bpy)(CO)3)3](OTf)3 (5, right) obtained from single-crystal X-ray structure determinations. Atoms are represented as 50% probability thermal ellipsoids.

Figure 2. Electronic absorption spectra of [Fe(pyacac)3(Re(deeb)-(CO)3)3](OTf)3 (3) (black trace) and [Al(pyacac)3(Re(deeb)(CO)3)3](OTf)3 (6) (blue trace) acquired in CH2Cl2 solution at 298 K. The dashed red trace corresponds to linear combination of the molar absorptivity profiles of the AlIII complex with that of Fe(pyacac)3 (inset).

(70) McCarthy, H. J.; Tocher, D. A. Polyhedron 1987, 6, 1421.


reflecting the electron donating/withdrawing ability of the bpy substituents. The $^1A_1 \rightarrow ^1MLCT$ absorption of the Re(deeb)(CO)$_3$ chromophore is evident in Figure 2 with $\lambda_{\text{max}}$ = 394 nm; as the substituents become progressively more electron donating (e.g., H for bpy and CH$_3$ for tmb) this feature systematically shifts to the blue and begins to overlap with the ligand-based absorptions in the ultraviolet (Supporting Information, Figure S1).

The presence of Fe$^{III}$ in complexes 1–3 gives rise to a new, broad absorption feature on the low-energy side of the Re$^{II}$-based charge-transfer band. The inset of Figure 2 shows the absorption spectrum of Fe(phacac)$_3$ which exhibits two strong transitions centered at 370 and 460 nm assigned as $^6A_1 \rightarrow ^6MLCT$ and $^6A_1 \rightarrow ^6LMCT$ transitions, respectively.$^{73,74}$ In complexes 1–3 the higher energy MLCT absorption is obscured by the more intense $^1A_1 \rightarrow ^1MLCT$ band of the Re$^{II}$ chromophore, but the low energy tail of the $^6A_1 \rightarrow ^6LMCT$ transition can be seen extending out to approximately 600 nm. A linear combination of the spectrum of the Al$^{III}$ analogue with that of Fe(phacac)$_3$ (dashed red line) confirms that the ground-state absorption spectra of these complexes can be viewed in terms of a superposition of contributions from the Re$^{II}$ and Fe$^{III}$ fragments.

**Steady-State and Time-Resolved Emission.** The AlRe$_3$ complexes represent an ideal model for dynamics that may occur in the corresponding ReFe$_3$ systems because of their similar structural features and the inability of Al$^{III}$ to engage in excited-state processes such as electron or energy transfer. Emission spectra for complexes 4–6 were acquired at room temperature in deoxygenated CH$_2$Cl$_2$ and are plotted in Supporting Information, Figure S2. The spectral profiles correspond well to previously reported photophysical studies of Re$^{II}$ polypyrpyridyl systems, with the emission assigned as a $^3MLCT \rightarrow ^1A_1$ transition.$^{75}$ The change in energy gap across the series due to differences in the electron donating/withdrawing ability of the substituents is reflected in the radiative quantum yields, dropping by a factor of $\sim$7 from complex 4 ($\Phi_r$ = 0.51) to complex 6 ($\Phi_r$ = 0.07); these values are comparable to those reported for the corresponding mononuclear Re$^{II}$ polypyrpyridyl derivatives.$^{46}$ Time-resolved emission data for complexes 4–6 could all be fit to single-exponential decay models. The kinetics reveal that the reduction in quantum yield is due primarily to an increase in the nonradiative decay rate for $^3MLCT$ relaxation ($k_{\text{nr}}$) as opposed to significant variations in radiative coupling to the ground state (Table 4). As with the quantum yields, the observed excited-state lifetimes and rate constants are all consistent with the assignment of $^3MLCT \rightarrow ^1A_1$ emission reported previously for the mononuclear Re$^{II}$ polypyrpyridyl derivates.$^{46,76}$

Steady-state emission spectra were also acquired for complexes 1–3. Although the data indicated significantly weaker emission from each of the FeRe$_3$ complexes as compared to their AlRe$_3$ analogues, suggesting efficient quenching by the Fe$^{III}$ core, the measured quantum yields were not reproducible. As mentioned in the Experimental Section, we believe this is due to the presence of a small amount of dissociated complex in solution caused by displacement of the phacac ligand from the Fe$^{III}$ core.

The lack of a readily identifiable steady-state signal from the intact FeRe$_3$ assemblies prompted the use of time-resolved methods to quantify the degree of excited-state quenching in complexes 1–3. A plot of the data obtained for complex 3 is shown in Figure 3; data for all three Fe$^{III}$-containing compounds are plotted in Supporting Information, Figure S3. The signal-to-noise ratio is relatively poor owing to a combination of virtually complete quenching of the Re$^{II}$-based $^3MLCT$ states coupled with radiative rate constants

![Table 4. Photophysical Data of Complexes 1–6](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda$ (nm)</th>
<th>$E_{\text{ex}}$ (cm$^{-1}$)</th>
<th>$\Phi_r$</th>
<th>$k_{\text{nr}}$ (s$^{-1}$)</th>
<th>$k_{\text{obs}}$ (s$^{-1}$)</th>
<th>$k_r$ (10$^5$ s$^{-1}$)</th>
<th>$k_{\text{nr}}$ (10$^6$ s$^{-1}$)</th>
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<td>[Fe(pyacac)(Re(deeb)(CO)$_3$)]$_3$(OTf)$_3$</td>
<td>4</td>
<td>562</td>
<td>19 900</td>
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<td>4.4 ± 0.2 × 10$^5$</td>
<td>2.3 ± 0.1</td>
<td>0.22 ± 0.01</td>
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<tr>
<td>[Fe(pyacac)(Re(bpy)(CO)$_3$)]$_3$(OTf)$_3$</td>
<td>5</td>
<td>566</td>
<td>18 700</td>
<td>0.16</td>
<td>1.8 ± 0.1 × 10$^6$</td>
<td>2.9 ± 0.1</td>
<td>1.5 ± 0.1</td>
</tr>
<tr>
<td>[Al(pyacac)(Re(deeb)(CO)$_3$)]$_3$(OTf)$_3$</td>
<td>6</td>
<td>624</td>
<td>16 800</td>
<td>0.07</td>
<td>4.3 ± 0.2 × 10$^5$</td>
<td>3.0 ± 0.1</td>
<td>4.0 ± 0.2</td>
</tr>
</tbody>
</table>

$^a$ Zero-point energy difference between $^1MLCT$ excited state and ground state based on spectral fitting analysis. $^b$ This value is expected to be identical to the corresponding Al$^{III}$ complex. $^c$ Values are not quoted because of the presence of an emissive impurity. See text for further details. $^d k_r = k_{\text{obs}}\Phi_r$. $^e k_{\text{nr}} = k_{\text{obs}} - k_r$. $^f k_r$ and $k_{\text{nr}}$ values are anticipated to be similar to the corresponding Al$^{III}$ complex.
that are on the order of $10^3 \text{ s}^{-1}$. Nevertheless, emission decays for each of the FeRe$_3$ complexes could be fit to single-exponential kinetics with $\tau_{\text{obs}} = 450 \pm 30 \text{ ps}$, $755 \pm 40 \text{ ps}$, and $2.5 \pm 0.1 \text{ ns}$ for complexes 1, 2, and 3, respectively (Table 4). These time constants are several orders of magnitude shorter than what was observed for the AlRe$_3$ model complexes, indicating that excited-state relaxation in complexes 1–3 is dominated by reaction with the Fe$_{III}$ core. The rate constant for the reaction is given by eq 5,

$$k_{\text{FeRe}_3} = k_{\text{FeRe}_3} - k_{\text{AlRe}_3}$$

(5)

where the values of $k_i$ and $k_{nr}$ for the 3MLCT excited state of a given FeRe$_3$ assembly are taken to be equivalent to the corresponding AlRe$_3$ model complex. Given the extensive quenching of the 3MLCT state as indicated by the time constant for decay in complexes 1–3, the observed lifetimes effectively correspond to the quenching time constants in all three cases.

**Mechanistic Considerations: Electron versus Energy Transfer Quenching.** Both electron and energy transfer processes can be envisioned to occur out of the Re$_I$-based complexes. Electron transfer would proceed as an oxidative quenching reaction to produce a Re$_{II}$/Fe$_{II}$ charge separated species. Re$_{III}$ → Re$_{II}$ oxidation and Fe$_{III}$ → Fe$_{II}$ reduction potentials for complexes 1–3 (Table 3), along with the zero-point energy gaps of the 3MLCT states ($E_{00}$) determined from fits of the emission spectra of the corresponding AlRe$_3$ analogues (Table 4), were used to determine the thermodynamic driving force for photoinduced electron transfer.$^{77,78}$ These calculations revealed that electron transfer is unfavorable for complexes 2 and 3 ($\sim 0$ and $+0.45 \text{ eV}$, respectively) and only slightly exothermic in the case of complex 1 ($-0.1 \text{ eV}$). The magnitude of $\Delta G^\text{ET}$ for complex 3 is prohibitively large, particularly given the observed rate constant of nearly $10^3 \text{ s}^{-1}$. In the case of complex 2, electron transfer is thermodynamically feasible; however, the fact that the quenching rate is only a factor of $\sim 3$ faster than what is observed for complex 3 suggests that both of these complexes are reacting via similar mechanisms, namely, energy transfer.

The fact that electron transfer is predicted to be exothermic in the case of complex 1 prompted further study. We therefore carried out time-resolved absorption measurements on [Fe(pyacac)$_3$(Re(tmb)(CO)$_3$)$_3$](OTf)$_3$ (1) in an effort to identify whether a charge-separated species was being formed upon $^1\text{A}_1 \rightarrow ^1\text{MLCT}$ excitation. The transient absorption spectroscopy of Re$_{II}$ polypyridyl complexes has been described by a number of workers.$^{79-86}$ Their excited-state spectra typically consist of a moderately intense feature in the ultraviolet corresponding to absorptions of the polypyridyl radical anion, as well as a transient bleach due to loss of the ground-state $^1\text{A}_1 \rightarrow ^1\text{MLCT}$ absorption. Additional absorptions can also be observed toward the red edge of the visible spectrum that are usually ascribed to bpy$^-$ transitions of the excited-state species. Consistent with these expectations, the differential absorption spectrum of [Al(pyacac)$_3$](Re(tmb)(CO)$_3$)$_3$](OTf)$_3$ (4) (Figure 4, top) exhibits transient absorptions at 370 and 760 nm that we assign to tmb$^-$ transitions. The hallmark for an excited-state electron transfer process in complex 1 would be a wavelength-dependence in the observed kinetics, namely, the loss of the tmb$^-$ features coupled with a persistence of the ground-state $^1\text{A}_1 \rightarrow ^1\text{MLCT}$ transitions.

![Figure 4. Top: nanosecond time-resolved differential absorption spectrum of [Al(pyacac)$_3$](Re(tmb)(CO)$_3$)$_3$](OTf)$_3$ (4) in room temperature CH$_2$Cl$_2$ solution. The spectrum was constructed from the amplitudes of fits to single-exponential decay kinetics at each probe wavelength following excitation at 355 nm. Bottom: time-resolved absorption data for [Fe(pyacac)$_3$(Re(tmb)(CO)$_3$)$_3$](OTf)$_3$ (1) in room-temperature CH$_2$Cl$_2$ solution at $\lambda_{\text{pump}} = 700 \text{ nm}$ following $\sim 100 \text{ fs}$ excitation at $\lambda_{\text{pump}} = 400 \text{ nm}$. The red solid line corresponds to a fit of the data to a single-exponential decay model with $\tau_{\text{obs}} = 400 \pm 30 \text{ ps}$.](image-url)
this is depicted graphically in Figure 5. We note that in
ν(CO) frequencies of the FeRe3 and AlRe3 analogues, as well as the fact that the absorption spectra of the FeRe3 assemblies can be represented in terms of a simple linear combination of its constituents (Figure 2). The applicability of the Förster mechanism is supported by the moderate degree of spectral overlap that exists between the ReI-based 3MLCT emission and the FeIII-based 6A1 → 9LMCT absorption: this is depicted graphically in Figure 5. We note that the qualitative changes in spectral overlap parallel the trend in rate constants for energy transfer determined from time-resolved emission measurements (Figure 4), which strongly implicates Förster transfer as the dominant quenching mechanism in this system.

Quantifying Förster Transfer. The spectral properties of the FeRe3 family of complexes combined with the structural rigidity of the system provides a rare opportunity to quantitatively apply Förster theory and compare calculated rates with those obtained experimentally. In addition to the overlap factor alluded to above, the rate of energy transfer is also sensitive to the relative orientation of the donor and acceptor transition dipoles (eq 3). An accurate determination of this quantity can be quite challenging. In one noteworthy example, Fleming and co-workers utilized time-dependent density functional theory (TD-DFT) to enable them to visualize the transition dipoles of peridinin, which in turn provided them with tremendous insights into the role geometry plays in facilitating energy transfer from the singlet excited state(s) of that system. Unfortunately, the complicated electronic structures of transition-metal containing systems do not easily lend themselves to a similarly detailed analysis, so more approximate methods must usually be employed.

An excellent example of this is that of Harriman and co-workers, in which Förster energy transfer dynamics in RuII and OsII polypyridine donor–acceptor complexes bridged by a rigid spiro-based spacer moiety were investigated. In their approach, energy-minimized structures were calculated for each molecule with the donor and acceptor transition dipole moments modeled along the six respective Ru–N and Os–N bond vectors. Using this geometric picture, calculations of donor–acceptor separations (RDA) and orientation factors (κ2) afforded a theoretical Förster rate constant that agreed very closely with the experimentally observed values. We have taken a similar approach for analyzing the FeRe3 family of complexes, albeit with slight differences in the physical description of the system. For example, we have chosen to approximate the donor and acceptor transition dipoles as bisecting the local C2 axes of the bpy’ and acac

ligands as opposed to them lying coincident with the metal–ligand bond vectors. In addition, the point of origin for the transition moment dipoles has been modeled to originate solely from the ligands involved in the donor and acceptor transitions. These choices are based largely on DFT calculations on [Ru(bpy)$_3$]$_2^{2+}$ by Daul et al.$^{94}$ and Gorelsky and Lever$^{95}$ that suggest the lowest energy excited state (3MLCT) is localized on the bpy ligands. In addition, Meyer and co-workers have shown that the majority of the amplitude of the thermalized 3MLCT wave function for complexes of the form fac-[Re(4,4′-X$_2$-bpy)(CO)$_3$(4-Et-py)](PF$_6$) (X = CH$_3$, H, and CO$_2$Et) is concentrated within the π* levels of the bpy′ ligand and less so along the Re–N bond vector.$^{65}$

Our model is illustrated in Charts 1–3. The emission dipoles of all three Re$^1$ donors (i.e., Re1, Re2, and Re3) are presented simultaneously for clarity in Chart 1, but only a single Re$^1$ moiety is considered to be involved in a given excited-state quenching event because of the low excitation photon flux used for the steady-state and time-resolved emission measurements (Chart 2). The presence of three $^6$A$_{1}$$\rightarrow$ $^6$LMCT absorption dipoles in the Fe$^{II}$ core gives rise to a set of vectors ($R_1$, $R_2$, and $R_3$) and angles ($\Theta_T$, $\Theta_D$, and $\Theta_A$) for each Re$^1$ fluorophore. The charge-transfer nature of the donor and acceptor transitions makes it difficult to place an exact point of origin for each, so distance and orientation factors were calculated for a range of possible loci for both the donor and acceptor (Chart 3). Thus, the individual Förster rate constants for a given fluorophore (Re1, Re2, or Re3) were determined for a particular origin associated with the donor (e.g., A, B, or C) interacting with a specific acceptor point associated with the Fe(pyacac)$_3$ core (D, E, and F, the Fe center). This approach yielded a total of 81 donor–acceptor interactions (27 for each Re$^1$ fluorophore), each being defined by specific $R_{DA}$ and $\kappa^2$ values that were evaluated based on the single-crystal X-ray structure data of complex 2. A complete list of the values of $R_{DA}$ and $\kappa^2$ used in our analysis can be found in the Supporting Information.

The analysis we have carried out is predicated on two critical assumptions: (1) that the variations in substituents on the peripheral bipyridine group do not significantly alter the metrics relevant for dipolar energy transfer (thereby allowing us to use the X-ray structure of complex 2 as the basis for analyzing all three FeRe$_3$ assemblies), and (2) that the geometry of each compound in solution is essentially unchanged from that determined by solid-state X-ray crystallography. The major influence of the bipyridyl substituents will be to shift the electron density associated with the excited state according to the electron donating/withdrawing ability of the group. This assertion is supported by structure

Table 5. Calculated Förster Rate Constants for [Fe(pyacac)(Re(trib-(CO))3)][OTf] (1), [Fe(pyacac)(Re(bpy))(CO)3][OTf] (2), and [Fe(pyacac)(Re(deeb)(CO)3)][OTf] (3)  

<table>
<thead>
<tr>
<th>interaction</th>
<th>complex 1a</th>
<th>complex 2b</th>
<th>complex 3c</th>
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<tr>
<td>Re1:LMCT1</td>
<td>3.6 × 1010</td>
<td>3.3 × 108</td>
<td>5.5 × 107</td>
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<td>Re1:LMCT2</td>
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<tr>
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<tr>
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</table>

*a Donor–acceptor through-space interaction as defined in the text and in Chart 3. *b R_{ij} and k_{ij} values derived from the single-crystal X-ray data for complex 2 using the geometries outlined in Charts 1 and 2. *c Rate of energy transfer calculated according to eqs 6a–6c. *d The overall rate of energy transfer given by (k_{Re1} + k_{Re2} + k_{Re3}).


Knight et al.

Figure 6. Energy level diagram depicting the excited-state dynamics of the FeRe3 assemblies described in this paper. The rate constants for 1MLCT → 3MLCT intersystem crossing and vibrational cooling within the 3MLCT state are based on the work of Vlček and co-workers (cf. 85), whereas the other time constants represent approximate values for complexes 1–6. k_{Re(ij)} values derive from the average of the nine possible donor–acceptor vectors defined by the point-dipole origins depicted in Chart 3. Table 5 lists all nine k_{Re(ij)} values for complexes 1–3 along with their average, (k_f), which take to be the overall theoretical rate constant from our model. It can be seen that there are variations in the calculated rates of energy transfer within each group of interactions owing to slight geometric differences at each Re-bpy site. Nevertheless, despite the lack of a quantitative picture of wave functions for the donor and acceptor charge-transfer states, we consider the level of agreement we have obtained between experiment and theory—less than a factor of 3 across the entire series—to be quite good and further supports our assignment of Förster transfer.

The results of this study allow us to construct a comprehensive picture of the excited-state energies and dynamics for these FeRe3 systems (Figure 6). The left side of Figure 6 is an energy level diagram for the relevant electronic states of the Re1-bpy' chromophore, along with kinetic pathways associated with the various excited states. Initial population of the 1MLCT excited state is followed by rapid intersystem crossing (k_{isc}) to the 1MLCT excited state. The thermalized triplet state can then undergo radiative (k_r) and nonradiative (k_{nr}) transitions to the 1A1 ground-state, or can be quenched by the Fe3II core via Förster energy transfer (k_{Förster}). The right side of Figure 6 shows the electronic structure of the Fe(pyacac)3 core, which contains charge-transfer (9LMCT) and ligand-field electronic excited states that are thermodynamically accessible from the 3MLCT manifold of the Re chromophore. Dipolar energy transfer results in the formation of a 9LMCT excited state within the Fe(pyacac)3 core, followed by nonradiative relaxation to the 6A1 ground-state of the Fe3II moiety.

Conclusions

The synthesis, structures, and photophysical properties of a series of donor–acceptor complexes based on Re1-bpyridine

donors and Fe$^{III}$-acac acceptors have been described. Steady-state and time-resolved emission spectroscopies indicated that the strongly emissive Re$^I$-based 3MLCT excited state was significantly quenched when compared to model complexes in which the Fe$^{III}$ center had been replaced by Al$^{III}$. The favorable overlap between the donor emission and acceptor absorption profiles coupled with a $\sim 10$ Å donor–acceptor separation, unfavorable driving forces for electron transfer, and the absence of features characteristic of charge separation in the transient absorption spectra allowed for an assignment of Förster (dipolar) energy transfer as the dominant excited-state reaction mechanism. The well-defined structural aspects of this system permitted a quantitative geometric analysis of the dipole–dipole coupling giving rise to the observed dynamics. The calculated energy transfer rate constants differed from the experimental values by less than a factor of 3, a level of agreement that is significantly better than what is typically encountered. In addition to providing quantitative support for Förster transfer in this system, this study also demonstrates the degree of accuracy that can be achieved if the metric details concerning dipole–dipole interactions can be explicitly described.

**Acknowledgment.** The authors wish to thank Professor Gary Blanchard for use of the time-correlated single photon counting spectrometer and for insightful discussions, as well as Allison Brown for help in the acquisition of the femtosecond time-resolved absorption data. This work was supported with funds from the National Science Foundation under Grant CHE-0616340.

**Supporting Information Available:** Electronic absorption spectra for complexes 1–6 (Figure S1), steady-state emission spectra for complexes 1–6 (Figure S2), and time-resolved emission spectra for complexes 1–6 (Figure S3). $R_{DA}$, $\Theta_T$, $\Theta_D$, $\Theta_A$, and $\kappa^2$ values calculated from the X-ray structural data of complex 2 for all A:D, B:D, and C:D interactions (Table S1), for all A:E, B:E, and C:E interactions (Table S2), and for all A:F, B:F, and C:F interactions (Table S3), as well as the corresponding calculated Förster rate constants (Tables S4–S6). Crystallographic data for complexes 2 and 5 in cif format are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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