

Angular Momentum Conservation in Dipolar Energy Transfer

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Conservation of angular momentum is a familiar tenet in science but has seldom been invoked to understand (or predict) chemical processes. We have developed a general formalism based on Wigner's original ideas concerning angular momentum conservation to interpret the photo-induced reactivity of two molecular donor-acceptor assemblies with physical properties synthetically tailored to facilitate intramolecular energy transfer. Steady-state and time-resolved spectroscopic data establishing excited-state energy transfer from a rhenium(I)-based charge-transfer state to a chromium(III) acceptor can be fully accounted for by Förster theory, whereas the corresponding cobalt(III) adduct does not undergo an analogous reaction despite having a larger cross-section for dipolar coupling. Because this pronounced difference in reactivity is easily explained within the context of the angular momentum conservation model, this relatively simple construct may provide a means for systematizing a broad range of chemical reactions.

Conservation of angular momentum appears to be a fundamental property of nature (1). It is widely manifest in settings as varied as astrophysics, in which the idea of coupled momenta can be used to infer the presence of satellites, and figure skating, where skaters spin faster and faster as they draw their arms in. In chemistry, the principle figures prominently in the interpretation of optical spectra. For example, conservation of spin angular momentum (2) forms the basis of the so-called spin selection rule whereby radiative transitions between two states of differing spin multiplicity are forbidden (3). A more familiar special case of this phenomenon is the (relatively) long lifetime of an electronic excited state with spin angular momentum different from that of the ground state. This condition leads to the observation of phosphorescence and has more recently found application in the development of organic light-emitting diodes (OLEDs) (4) as well as the creation of charge-separated excited states that form the conceptual underpinning of many current approaches to solar energy conversion (5).

In 1927, Wigner introduced the notion of spin conservation in chemical reactions (6). According to his generalization of the specific examples just described, a chemical reaction would be designated "spin-allowed" if the spin angular momentum space spanned by the reactants intersects the spin angular momentum space spanned by the products. Although not explicitly stated in Wigner's original presentation, the relative energies of the spin-coupled reactant-product states must also be considered in order to define the thermodynamic viability of the reaction in question. A straightforward way to illustrate this idea is to

envision a generic energy transfer reaction between an electronically excited donor species (D^*) and an energy acceptor (A):



Focusing on the energy transfer step, the total spin angular momenta spanned by the coupled reactants (S_T^R) and products (S_T^P) can be described according to

$$|S_T^R| = S_{D^*} + S_A = |S_{D^*} + S_A|, \\ |S_{D^*} + S_A - 1|, \dots, |S_{D^*} - S_A| \quad (2)$$

$$|S_T^P| = S_D + S_{A^*} = |S_D + S_{A^*}|, \\ |S_D + S_{A^*} - 1|, \dots, |S_D - S_{A^*}| \quad (3)$$

where $|S_D|$, $|S_{D^*}|$, $|S_A|$, and $|S_{A^*}|$ represent the magnitudes of the spin angular momenta of the ground and excited states of the donor and acceptor, respectively. This formalism is identical to the vector coupling of spin angular momenta used to describe magnetic exchange interactions among weakly coupled paramagnetic species (7). In the present context, a spin-allowed reaction is possible if (i) there exists a value of S common to both the reactant and product manifolds (i.e., $\Delta S = 0$ for the reaction), and (ii) the energy of that common state is lower in the product manifold ($\Delta G < 0$). This concept has been invoked explicitly for the interpretation of collisional fragmentation reactions in the gas phase (8–10) and more implicitly in the context of spin effects in chemical reactions in general (11–16). Here, we seek to implement the formalism just described in order to broaden the perceived scope of angular momentum conservation as a tool for the development and interpretation of photo-induced excited-state dynamics. Specifically, we have prepared two isostructural donor-acceptor assemblies synthetically tailored to undergo facile intramolecular

dipolar energy transfer. The stark difference in observed reactivity between these two systems can be readily explained within the framework of the model just described, thereby illustrating the utility of this formalism in the context of one of the simplest and most widely exploited excited-state reactions.

The chemical structure of the donor-acceptor system is outlined in Fig. 1. Excitation of the Re-bpy chromophore in the near-ultraviolet populates a singlet metal-to-ligand charge transfer state ($^1\text{MLCT}$); this state undergoes rapid (<100 fs) intersystem crossing to a lower-lying triplet state ($^3\text{MLCT}$) that, in the absence of a suitable acceptor, persists in deoxygenated solution for ~600 ns (17). We have previously reported on the propensity of this compositional motif to exhibit dipolar energy transfer reactivity. In the case of the iron-based adduct (i.e., $M = \text{Fe}^{\text{III}}$), Förster theory (18) quantitatively accounted for the energy transfer process from the Re-bpy $^3\text{MLCT}$ donor to a $^6\text{LMCT}$ (ligand-to-metal charge transfer) state of the $\text{Fe}(\text{pyacac})_3$ core (19). The present study involves a comparison of reactivity in isostructural compounds in which Cr^{III} and Co^{III} replace Fe^{III} as the acceptors; a Ga^{III} derivative was also prepared to serve as a reference because of its inability to engage in energy or electron transfer reactions in this setting (20, 21).

The $^1A_1 \rightarrow ^1\text{MLCT}$ absorption of $[\text{Cr}(\text{pyacac})_3\{\text{Re}(\text{bpy})(\text{CO})_3\}_3]^{3+}$ (CrRe_3 , 1) appears as a pronounced shoulder with $\lambda_{\text{max}} \approx 375$ nm (Fig. 2A); a significantly weaker feature near 580 nm is assigned to the $^4A_2 \rightarrow ^4T_2$ ligand-field transition of the central Cr^{III} ion (Fig. 2A, inset). It is clear that $^3\text{MLCT} \rightarrow ^1A_1$ emission from the Re-bpy moiety possesses excellent spectral overlap with the ligand-field band of the Cr^{III} chromophore, thus predisposing the system for dipolar energy transfer from the periphery to the core of the assembly. A similar situation pertains to $[\text{Co}(\text{pyacac})_3\{\text{Re}(\text{bpy})(\text{CO})_3\}_3]^{3+}$ (CoRe_3 , 2) in which the Re-bpy emission is expected to couple to the $^1A_1 \rightarrow ^1T_1$ absorption of the low-spin Co^{III} ion centered at $\lambda_{\text{max}} = 610$ nm (Fig. 2B).

Excitation of the CrRe_3 assembly at 375 nm gives rise to a very weak steady-state emission characteristic of the Re-bpy luminophore (Fig. 3A). The data are relatively noisy because of significant attenuation of the signal for the CrRe_3 assembly relative to that of the Ga^{III} -containing model complex (Fig. 3A, inset). The factor of 100 decrease in the observed lifetime of the Re-based $^3\text{MLCT}$ excited state (Table 1) quantitatively establishes dynamic quenching of the $^3\text{MLCT}$ state due to the presence of Cr^{III} (22). Although this observation serves to indicate a reaction between the charge-transfer excited state and the $\text{Cr}(\text{pyacac})_3$ core, it is not mechanistically diagnostic: Electron transfer, dipolar energy transfer, and exchange energy transfer could all manifest these dynamics. Electrochemical measurements allowed for unambiguous assignments of the Re-, bpy-, and Cr^{III} -based redox processes (table S1); subsequent

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application of the Rehm-Weller equation (23) in conjunction with spectral fitting of the emission profile (24) rules out an electron transfer mechanism due to the endothermicity of both reductive and oxidative quenching of the Re-based excited state by Cr^{III} .

Excited-state energy transfer from the $^3\text{MLCT}$ state of the Re-bpy chromophore to the $\text{Cr}(\text{pyacac})_3$ core should result in the eventual formation of the lower-energy ^2E state of the Cr^{III} ion (25). The $^2\text{E} \rightarrow ^4\text{A}_2$ phosphorescence is generally not observed in room-temperature fluid solution of Cr^{III} complexes but often becomes more intense in low-temperature optical glasses because of the sup-

pression of nonradiative decay dynamics in a rigid medium (26). The emission profile obtained after $^1\text{A}_1 \rightarrow ^1\text{MLCT}$ excitation of the Re chromophore at 80 K is identical to that observed after $^4\text{A}_2 \rightarrow ^4\text{T}_2$ excitation of the $\text{Cr}(\text{phacac})_3$ model compound (fig. S2). Moreover, the intensity of the 80 K emission from the CrRe_3 complex cannot be accounted for by differential excitation of the Cr^{III} core directly, confirming energy transfer as the dominant excited-state reaction pathway in the CrRe_3 assembly (27).

The $\sim 10 \text{ \AA}$ separation between the Re-bpy group and the Cr^{III} center (28) effectively rules out an exchange mechanism because of its ex-

ponential dependence on distance (29). The rate constant for dipolar energy transfer is given by

$$k_{E_{nT}} = \frac{9000 \cdot \ln(10) \cdot \kappa^2 \cdot \Phi_D \cdot J}{128 \cdot \pi^5 \cdot \eta^4 \cdot N_A \cdot \tau_D \cdot R^6} \quad (4)$$

where κ^2 is the dipole orientation factor, Φ_D is the donor quantum yield, η is the refractive index of the solvent, N_A is Avogadro's number, τ_D is the excited-state lifetime of the donor, R is the donor-acceptor separation, and J is the spectral overlap integral (18, 19). This latter term can be evaluated from the spectroscopic properties of the system according to

$$J = \int_0^\infty \frac{\bar{F}_D(\bar{\nu}) \bar{\epsilon}_A(\bar{\nu})}{\bar{\nu}^4} d\bar{\nu} \quad (5)$$

where \bar{F}_D is the emission spectrum of the donor normalized to unity and $\bar{\epsilon}_A$ is the absorption profile of the acceptor in units of molar absorptivity. The overlap integral essentially quantifies the resonance condition necessary for dipole-dipole coupling graphically illustrated in the insets of Fig. 2, A and B. The emission profile of the Re-bpy luminophore is easily tuned by changing the substituents on the bipyridyl ligand; an observed correlation between the rate constant for energy transfer and the spectral overlap integral for several derivatives of the Re-bpy' luminophore (fig. S3 and table S2) further establishes this mechanistic assignment.

The photophysics exhibited by the CrRe_3 assemblies stands in stark contrast to the data acquired on the Co^{III} analog. As was the case with the CrRe_3 assembly, electrochemical data indicate that both oxidative and reductive quenching

Fig. 1. Molecular structure of the cation of $[\text{M}(\text{pyacac})_3\{\text{Re}(\text{bpy})(\text{CO})_3\}_3](\text{OTf})_3$ prepared for this study. **1**, $\text{M} = \text{Cr}^{\text{III}}$; **2**, $\text{M} = \text{Co}^{\text{III}}$; **3**, $\text{M} = \text{Ga}^{\text{III}}$.

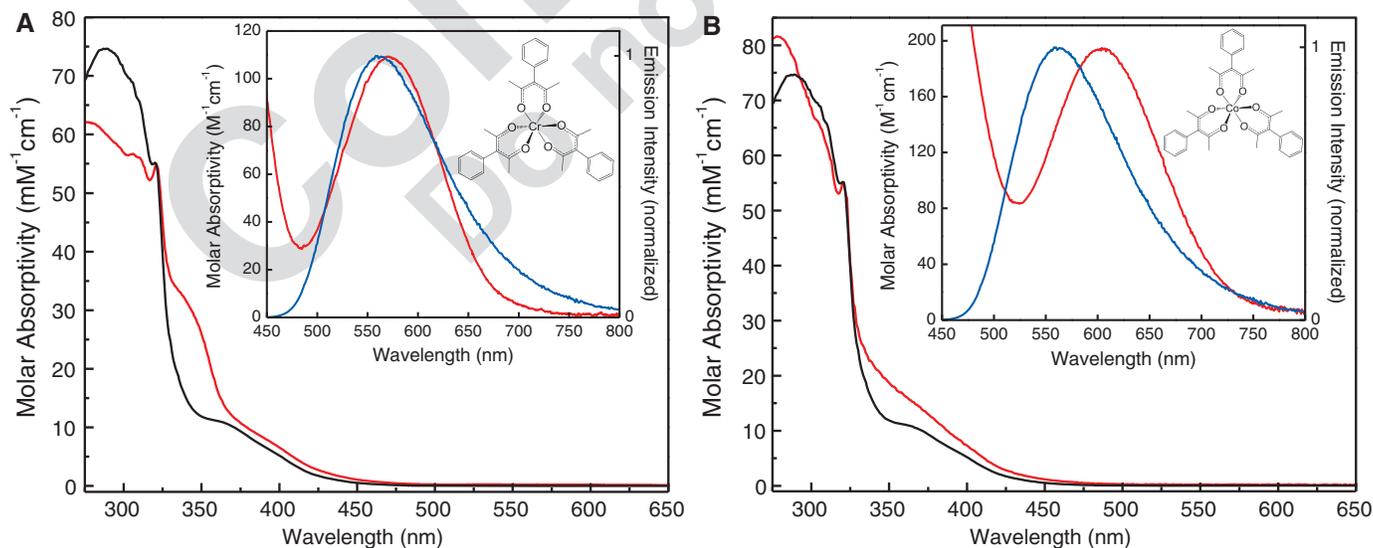
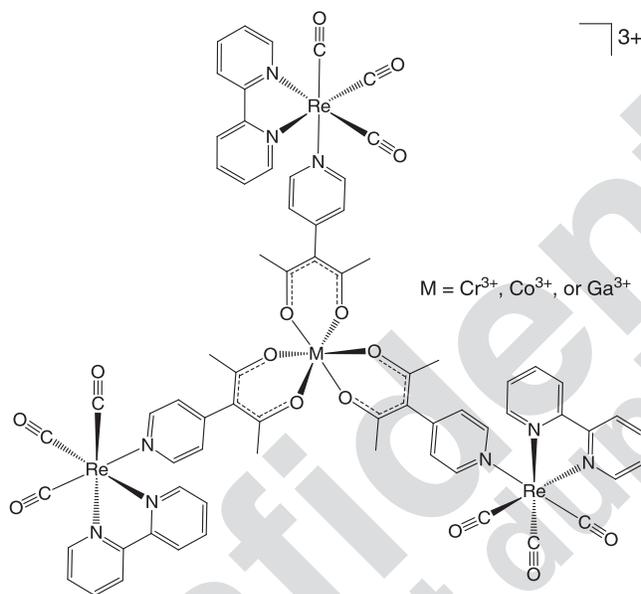


Fig. 2. (A) Electronic absorption spectra of $[\text{Cr}(\text{pyacac})_3\{\text{Re}(\text{bpy})(\text{CO})_3\}_3](\text{OTf})_3$ (CrRe_3 , **1**, red trace) and $[\text{Ga}(\text{pyacac})_3\{\text{Re}(\text{bpy})(\text{CO})_3\}_3](\text{OTf})_3$ (GaRe_3 , **3**, black trace). Inset: Emission spectrum of GaRe_3 (**3**, blue trace), scaled to the 580-nm peak intensity of the superimposed electronic absorption spectrum of $\text{Cr}(\text{phacac})_3$ (red trace); the latter was used as a surrogate for the $\text{Cr}(\text{pyacac})_3$ core. Spectra were acquired in CH_2Cl_2 solutions at room temperature. (B) Electronic absorp-

tion spectra of $[\text{Co}(\text{pyacac})_3\{\text{Re}(\text{bpy})(\text{CO})_3\}_3](\text{OTf})_3$ (CoRe_3 , **2**, red trace) and GaRe_3 (**3**, black trace). Inset: Emission spectrum of GaRe_3 (**3**, blue trace), scaled to the 610-nm peak intensity of the superimposed electronic absorption spectrum of $\text{Co}(\text{phacac})_3$ (red trace); the latter was used as a surrogate for the $\text{Co}(\text{pyacac})_3$ core. Spectra were acquired in CH_2Cl_2 solutions at room temperature.

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of the Re-based $^3\text{MLCT}$ excited state by the Co(pyacac) $_3$ core are significantly endothermic (table S1). The inset of Fig. 2B clearly shows substantial overlap between the emission spectrum of the Re-bpy luminophore and the ligand-field absorption of the Co(pyacac) $_3$ acceptor; the larger oscillator strength associated with the $^1\text{A}_1 \rightarrow ^1\text{T}_1$ absorption relative to the $^4\text{A}_2 \rightarrow ^4\text{T}_2$

absorption of Cr^{III} actually translates to a factor of 2 increase in the spectral overlap integral (Table 1), which should enhance the rate of dipolar energy transfer in the CoRe $_3$ system. Both steady-state and time-resolved emission data are completely at odds with these expectations: As shown in Fig. 3B and Table 1, the emission lifetime and quantum yield of the $^3\text{MLCT}$ excited state of $[\text{Co}(\text{pyacac})_3\{\text{Re}(\text{bpy})(\text{CO})_3\}_3]^{3+}$ are identical to that of the GaRe $_3$ model complex, an observation that indicates a complete absence of reactivity between the charge-transfer excited state of the Re-bpy fragment and the Co^{III} core.

An analysis of the spin-coupled pathways for dipolar energy transfer available in these two systems provides a surprisingly simple explanation for this marked difference in photophysical behavior (Fig. 4). In both compounds, the $^3\text{MLCT}$ excited state has a spin multiplicity of $|S_{\text{D}^*}| = 1$; energy transfer from this state to the M(pyacac) $_3$ core results in reformation of the singlet ground

Table 1. Photophysical data for $[\text{M}(\text{pyacac})_3\{\text{Re}(\text{bpy})(\text{CO})_3\}_3](\text{OTf})_3$ assemblies. Spectral overlap integral is in units of $10^{-16} \text{ M}^{-1} \text{ cm}^3$ as determined by Eq. 5. Radiative quantum yield Φ_r was determined by a relative measurement of steady-state emission. Rate constants for energy transfer are defined as $k_{E,T} = k_{\text{obs}}^{\text{MRe}_3} - k_{\text{obs}}^{\text{GaRe}_3}$, where $k_{\text{obs}}^{\text{MRe}_3}$ and $k_{\text{obs}}^{\text{GaRe}_3}$ are the measured rate constants for excited-state decay for the MRe $_3$ (where M = Cr^{III} or Co^{III}) and GaRe $_3$ complexes, respectively. Rate constants for energy transfer are calculated according to Eq. 4.

Compound	Spectral overlap integral (J)	Φ_r	$k_{E,T}$ (obs.) (s^{-1})	$k_{E,T}$ (calc.) (s^{-1})
$[\text{Cr}(\text{pyacac})_3\{\text{Re}(\text{bpy})(\text{CO})_3\}_3](\text{OTf})_3$ (1)	8.07	$<10^{-3}$	$1.7 (\pm 0.2) \times 10^8$	0.4×10^8
$[\text{Co}(\text{pyacac})_3\{\text{Re}(\text{bpy})(\text{CO})_3\}_3](\text{OTf})_3$ (2)	16.6	$0.16 \pm 0.02^*$	$<10^5$	1.7×10^8
$[\text{Ga}(\text{pyacac})_3\{\text{Re}(\text{bpy})(\text{CO})_3\}_3](\text{OTf})_3$ (3)	†	0.17 ± 0.02	†	†

*Corrected for differential absorption of Co^{III} core versus Re-bpy moiety. See (21) for further details. †The GaRe $_3$ assembly is a reference compound for the CrRe $_3$ and CoRe $_3$ complexes. The Ga^{III} core has no visible absorptions (hence $J = 0$) and does not engage in dipolar energy transfer reactions.

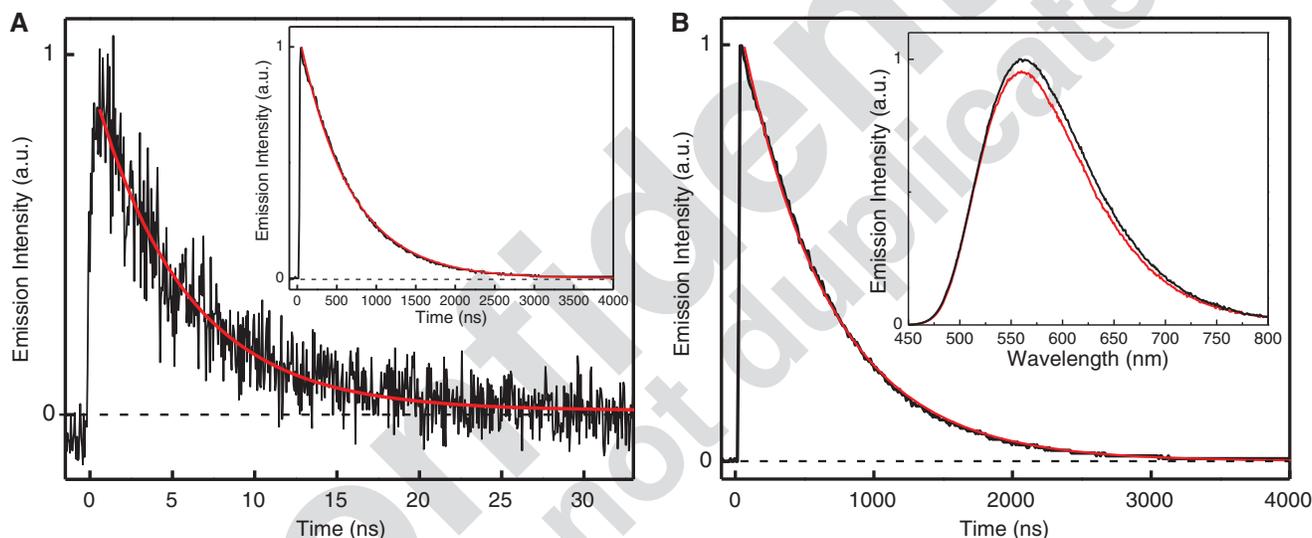


Fig. 3. (A) Time correlated single-photon counting data for CrRe $_3$ (**2**) at $\lambda = 580$ nm after excitation at 375 nm, fit to a single-exponential decay model (red line) with $\tau_{\text{obs}} = 4.8 \pm 0.2$ ns. Inset: Nanosecond time-resolved emission data for GaRe $_3$ (**3**) at $\lambda = 580$ nm after excitation at 400 nm, fit to a single-exponential decay model (red line) with $\tau_{\text{obs}} = 630 \pm 30$ ns. All data were collected at room temperature in deoxygenated CH_2Cl_2 solutions. (B) Nano-

second time-resolved emission data for CoRe $_3$ (**2**) at $\lambda = 580$ nm after excitation at 400 nm, fit to a single-exponential decay model (red line) with $\tau_{\text{obs}} = 640 \pm 30$ ns. Inset: Steady-state emission spectra for CoRe $_3$ (**2**, red trace) and GaRe $_3$ (**3**, black trace). The emission profile for the CoRe $_3$ complex has been corrected for the differential absorption of Co^{III} versus the Re-bpy moiety (21). All data were acquired at room temperature in deoxygenated CH_2Cl_2 solutions.

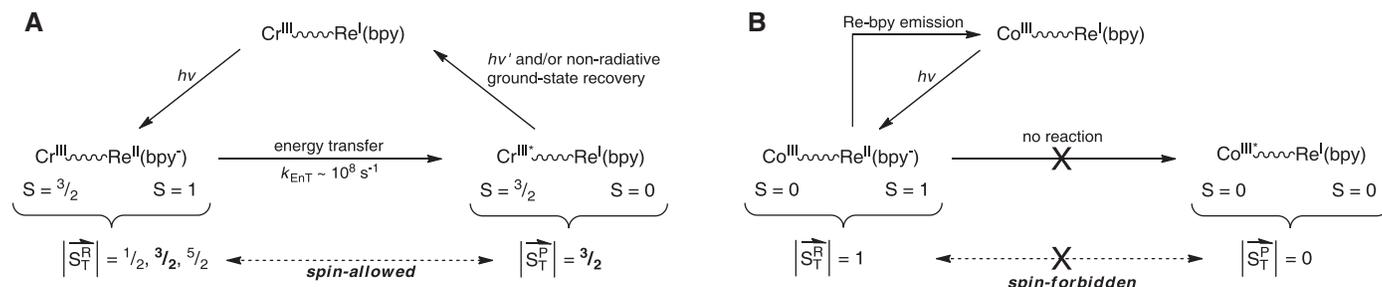


Fig. 4. Reaction schemes for dipolar energy transfer in (A) $[\text{Cr}(\text{pyacac})_3\{\text{Re}(\text{bpy})(\text{CO})_3\}_3](\text{OTf})_3$ and (B) $[\text{Co}(\text{pyacac})_3\{\text{Re}(\text{bpy})(\text{CO})_3\}_3](\text{OTf})_3$. In the case of the Cr^{III} adduct, the commonality of $S = 3/2$ states in both the reactant and product manifolds provides a pathway for spin-allowed energy transfer. The absence of

a corresponding situation in the Co^{III} -containing assembly explains the lack of reactivity exhibited by $[\text{Co}(\text{pyacac})_3\{\text{Re}(\text{bpy})(\text{CO})_3\}_3](\text{OTf})_3$ despite favorable spectral overlap and lends support to the angular momentum conservation formalism developed herein.

state of the Re-bpy moiety ($|S_D| = 0$). In the case of $M = \text{Cr}^{\text{III}}$, the ${}^4\text{A}_2$ ground state ($|S_A| = 3/2$) creates a spin manifold in the reactant angular momentum space spanning $|S_R| = 1/2, 3/2, \text{ and } 5/2$; this requires coupling to an excited state of the acceptor characterized by $|S_A| = 1/2, 3/2, \text{ or } 5/2$ in order to realize a spin-allowed pathway. Angular momentum conservation is clearly satisfied with the ${}^4\text{T}_2$ excited state of the Cr^{III} core ($|S_{A^*}| = 3/2$), as are thermodynamic considerations by virtue of the resonant condition that exists between the Re-bpy emission and the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ absorption. Thus, dipolar energy transfer can proceed through the commonality of $S = 3/2$ states in both the reactants and products, and excited-state quenching of the ${}^3\text{MLCT}$ emission is observed. Upon replacement of Cr^{III} by Co^{III} , the thermodynamics of energy transfer are essentially unchanged; however, the low-spin d^6 configuration of the $\text{Co}(\text{pyacac})_3$ core fundamentally alters the momentum conservation condition. Specifically, the phosphorescent nature of the ${}^3\text{MLCT} \rightarrow {}^1\text{A}_1$ emission requires coupling to an excited state of the Co^{III} having $|S_{A^*}| = 1$, not $|S_{A^*}| = 0$, which defines the ${}^1\text{A}_1 \rightarrow {}^1\text{T}_1$ absorption. Dipolar energy transfer is therefore spin-forbidden for the CoRe_3 assembly, thus giving rise to emission from the Re-bpy luminophore that is indistinguishable from that of the Ga^{III} model complex.

Although the chemical systems just described were designed specifically to illustrate the principle of angular momentum conservation in dipolar energy transfer, it does not appear to us that this formalism should be limited to energy transfer. In principle, a parallel set of expressions for any chemical reaction could be drafted in which consideration of reactant and product angular momenta serves to differentiate various thermo-

dynamically viable pathways. It seems likely that the issues raised herein will manifest more readily in inorganic rather than organic systems because of the broader array of spin states generally accessible in such compounds; however, we believe that the underlying concepts reflected in this simple formalism and experimentally verified in our study should be generalizable across a wide array of chemical processes.

References and Notes

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28. Estimated from the x-ray structure of $[\text{Ga}(\text{pyacac})_3(\text{Re}(\text{bpy})(\text{CO})_3)_3](\text{OTf})_3$ (21).
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Supporting Online Material

www.sciencemag.org/cgi/content/full/334/ISSUE/PAGE/DC1
Materials and Methods
Figs. S1 to S7
Tables S1 to S5
References (30–39)

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