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Angular Momentum Conservation in Dipolar Energy Transfer

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Supporting Online Material

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Angular Momentum Conservation in Dipolar Energy Transfer

Dong Guo,* Troy E. Knight,* James K. McCusker†

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 familiar manifestation 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 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*) whereby a process 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):

$$\mathrm{D}+\mathrm{A}\xrightarrow{h\nu}\mathrm{D}^*+\mathrm{A}\xrightarrow[\text{energy transfer}]{}\mathrm{D}+\mathrm{A}^* \qquad (1)$$

Focusing on the energy transfer step, the total spin angular momenta spanned by the coupled reactants ($\mathbf{S}_\mathrm{T}^\mathrm{R}$) and products ($\mathbf{S}_\mathrm{T}^\mathrm{P}$) can be described according to

$$|\mathbf{S}_\mathrm{T}^\mathrm{R}| = \mathbf{S}_{\mathrm{D}*} + \mathbf{S}_\mathrm{A} = |S_{\mathrm{D}*}+S_\mathrm{A}|,\ |S_{\mathrm{D}*}+S_\mathrm{A}-1|,\ldots,|S_{\mathrm{D}*}-S_\mathrm{A}| \qquad (2)$$

$$|\mathbf{S}_\mathrm{T}^\mathrm{P}| = \mathbf{S}_\mathrm{D} + \mathbf{S}_{\mathrm{A}*} = |S_\mathrm{D}+S_{\mathrm{A}*}|,\ |S_\mathrm{D}+S_{\mathrm{A}*}-1|,\ldots,|S_\mathrm{D}-S_{\mathrm{A}*}| \qquad (3)$$

where $|S_\mathrm{D}|$, $|S_{\mathrm{D}*}|$, $|S_\mathrm{A}|$, and $|S_{\mathrm{A}*}|$ 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

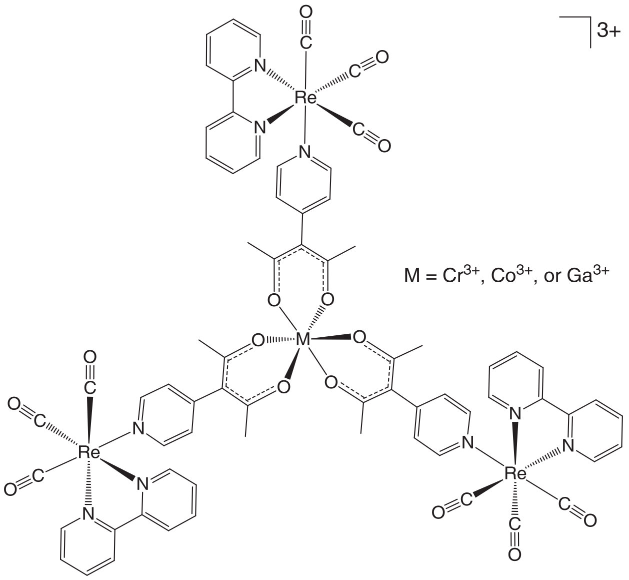

Fig. 1. Molecular structure of the cation of [M(pyacac)$_3${Re(bpy)(CO)$_3$}$_3$](OTf)$_3$ prepared for this study. **1**, M = Cr$^{\mathrm{III}}$; **2**, M = Co$^{\mathrm{III}}$; **3**, M = Ga$^{\mathrm{III}}$.

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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}MLCT); this state undergoes rapid (<100 fs) intersystem crossing to a lower-lying triplet state (^{3}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 = Fe^{III}), Förster theory (*18*) quantitatively accounted for the energy transfer process from the Re-bpy ^{3}MLCT donor to a ^{6}LMCT (ligand-to-metal charge transfer) state of the Fe(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 $^1A_1 \rightarrow {}^1$MLCT absorption of [Cr(pyacac)$_3$-{Re(bpy)(CO)$_3$}$_3$]$^{3+}$ (CrRe$_3$, **1**) appears as a pronounced shoulder at $\lambda_{max} \approx 375$ nm (Fig. 2A); a 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}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 [Co(pyacac)$_3${Re(bpy)(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 $\lambda_{max} = 610$ nm (Fig. 2B).

Excitation of the CrRe$_3$ assembly at 375 nm gives rise to very weak emission characteristic of the Re-bpy luminophore (Fig. 3A). The factor of 100 decrease in the observed lifetime of the Re-based ^{3}MLCT excited state relative to that of the Ga-containing model complex (Table 1) quantitatively establishes dynamic quenching of the ^{3}MLCT state attributable to the presence of Cr^{III} (*22*). Although this observation serves to indicate a reaction between the charge-transfer excited state and the Cr(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 application of the Rehm-Weller equation (*23*) in conjunction with spectral fitting of the emission profile (*24*) rules out an electron transfer mechanism because of the endothermicity of both reductive and oxidative quenching of the Re-based excited state by Cr^{III}.

Excited-state energy transfer from the ^{3}MLCT state of the Re-bpy chromophore to the Cr(pyacac)$_3$ core should result in the eventual formation of the lower-energy ^{2}E excited state of the Cr^{III} ion (*25*). The $^2E \rightarrow {}^4A_2$ phosphorescence is generally not observed in room-temperature fluid solutions of Cr^{III} complexes but often becomes more intense in low-temperature optical glasses because of the suppression of nonradiative decay dynamics in a rigid medium (*26*). The emission profile obtained after $^1A_1 \rightarrow {}^1$MLCT excitation of the Re chromophore at 80 K is identical to that observed after $^4A_2 \rightarrow {}^4T_2$ excitation of the Cr(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 ~10 Å separation between the Re-bpy group and the Cr^{III} center (*28*) effectively rules out an exchange mechanism because of its exponential dependence on distance (*29*). The rate constant for dipolar energy transfer is given by

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

where κ^2 is the dipole orientation factor, Φ_D is the radiative quantum yield of the donor, 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

$$J = \int_0^\infty \frac{\overline{F}_D(\bar{\nu})\,\bar{\varepsilon}_A(\bar{\nu})}{\bar{\nu}^4}\,d\bar{\nu} \qquad (5)$$

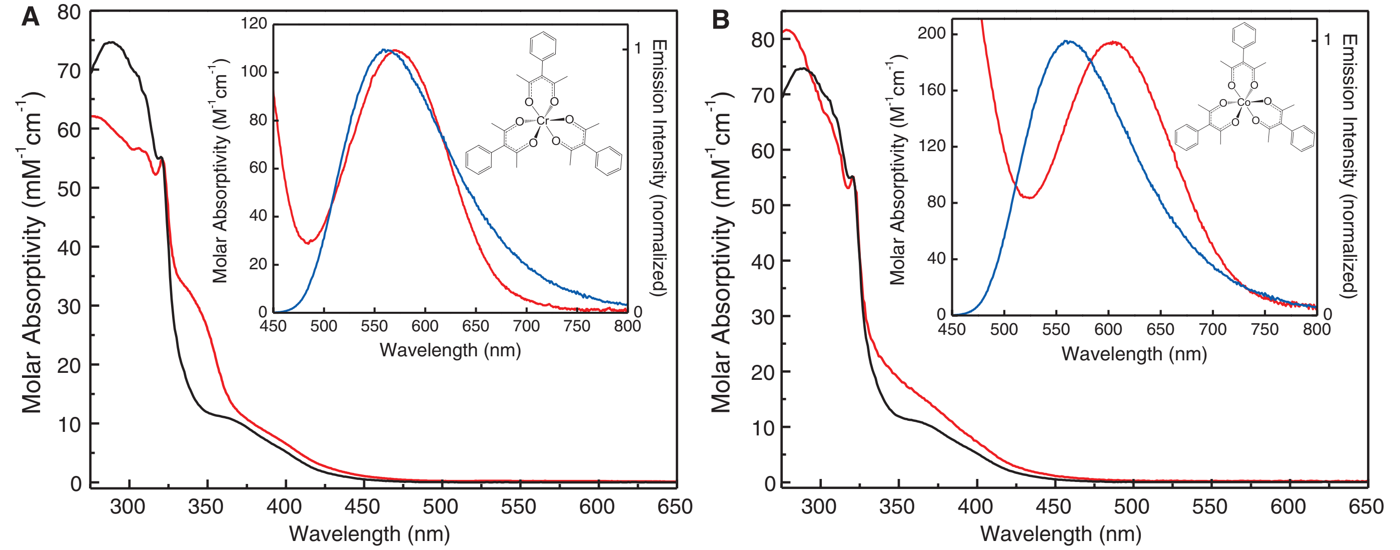

Fig. 2. (**A**) Electronic absorption spectra of [Cr(pyacac)$_3${Re(bpy)(CO)$_3$}$_3$](OTf)$_3$ (CrRe$_3$, **1**, red trace) and [Ga(pyacac)$_3${Re(bpy)(CO)$_3$}$_3$](OTf)$_3$ (GaRe$_3$, **3**, black trace). Inset: Emission spectrum of GaRe$_3$ (**3**, blue trace), scaled to the 580-nm peak intensity of the superimposed electronic absorption spectrum of Cr(phacac)$_3$ (red trace); the latter was used as a surrogate for the Cr(pyacac)$_3$ core. Spectra were acquired in CH$_2$Cl$_2$ solutions at room temperature. (**B**) Electronic absorption spectra of [Co(pyacac)$_3${Re(bpy)(CO)$_3$}$_3$](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 Co(phacac)$_3$ (red trace); the latter was used as a surrogate for the Co(pyacac)$_3$ core. Spectra were acquired in CH$_2$Cl$_2$ solutions at room temperature.

where $\overline{F}_D$ is the area-normalized emission spectrum of the donor and $\overline{\varepsilon}_A$ 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 of the Re-based ^{3}MLCT excited state by the Co(pyacac)$_3$ core are 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 $^1A_1 \rightarrow {}^1T_1$ absorption relative to the $^4A_2 \rightarrow {}^4T_2$ 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

Table 1. Photophysical data for [M(pyacac)$_3${Re(bpy)(CO)$_3$}$_3$](OTf)$_3$ assemblies. Spectral overlap integral is in units of 10^{-16} M^{-1} 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 $k_{E_nT} = k_{obs}^{MRe_3} - k_{obs}^{GaRe_3}$, where $k_{obs}^{MRe_3}$ and $k_{obs}^{GaRe_3}$ 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_nT} (obs.) (s^{-1})	k_{E_nT} (calc.) (s^{-1})
[Cr(pyacac)$_3${Re(bpy)(CO)$_3$}$_3$](OTf)$_3$ (**1**)	8.07	$<10^{-3}$	1.7 (±0.2) × 10^8	0.4 × 10^8
[Co(pyacac)$_3${Re(bpy)(CO)$_3$}$_3$](OTf)$_3$ (**2**)	16.6	0.16 ± 0.02*	$<10^5$	1.7 × 10^8
[Ga(pyacac)$_3${Re(bpy)(CO)$_3$}$_3$](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.

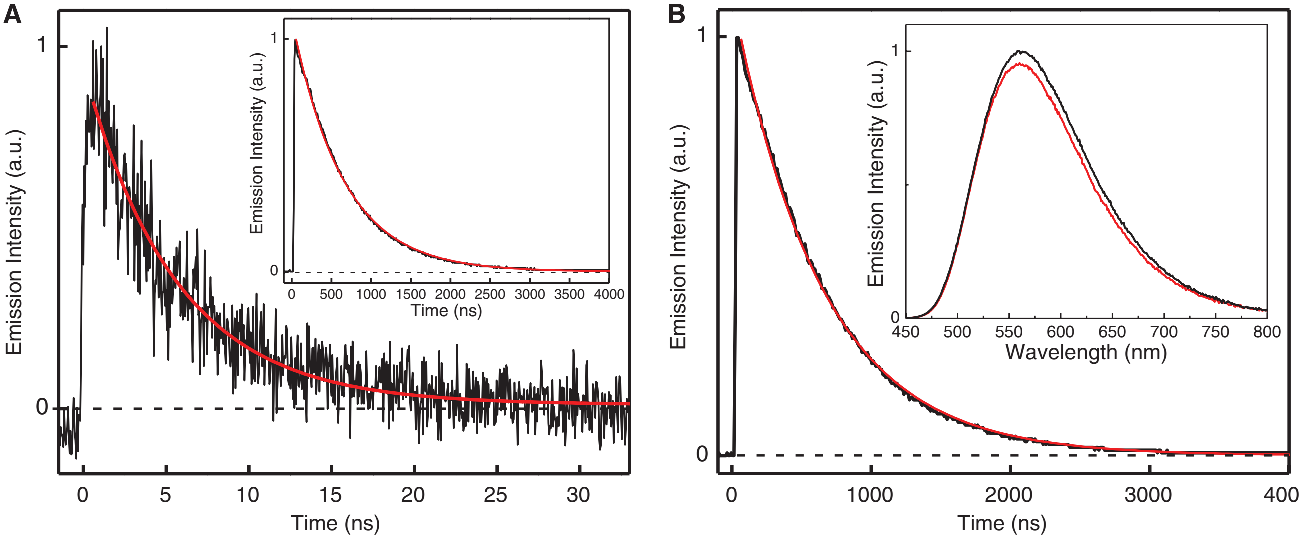

Fig. 3. (**A**) Time-correlated single-photon counting data for CrRe$_3$ (**1**) at λ = 580 nm after excitation at 375 nm, fit to a single-exponential decay model (red line) with τ_{obs} = 4.8 ± 0.2 ns. Inset: Nanosecond time-resolved emission data for GaRe$_3$ (**3**) at λ = 580 nm after excitation at 400 nm, fit to a single-exponential decay model (red line) with τ_{obs} = 630 ± 30 ns. All data were collected at room temperature in deoxygenated CH$_2$Cl$_2$ solutions. (**B**) Nanosecond time-resolved emission data for CoRe$_3$ (**2**) at λ = 580 nm after excitation at 400 nm, fit to a single-exponential decay model (red line) with τ_{obs} = 640 ± 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$_2$Cl$_2$ solutions.

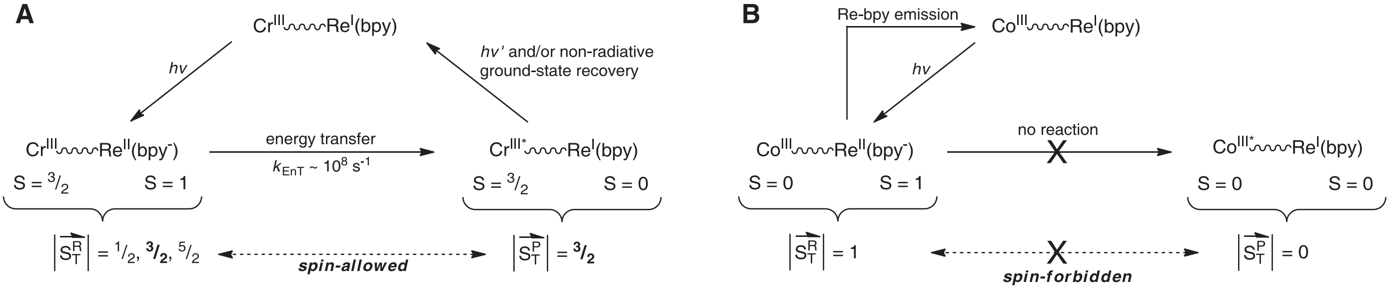

Fig. 4. Reaction schemes for dipolar energy transfer in (**A**) [Cr(pyacac)$_3${Re(bpy)(CO)$_3$}$_3$](OTf)$_3$ and (**B**) [Co(pyacac)$_3${Re(bpy)(CO)$_3$}$_3$](OTf)$_3$. In the case of the Cr^{III} adduct, the commonality of S = $^3/_2$ states in both the reactant and product manifolds provides a pathway for spin-allowed energy transfer. The absence of a corresponding situation in the Co^{III}-containing assembly explains the lack of reactivity exhibited by [Co(pyacac)$_3${Re(bpy)(CO)$_3$}$_3$](OTf)$_3$ despite favorable spectral overlap and lends support to the angular momentum conservation formalism developed herein.

Fig. 3B and Table 1, the emission lifetime and quantum yield of the ^{3}MLCT excited state of $[Co(pyacac)_3\{Re(bpy)(CO)_3\}_3]^{3+}$ 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}MLCT excited state has a spin multiplicity of $|S_{D*}| = 1$; energy transfer from this state to the M(pyacac)$_3$ core results in reformation of the singlet ground state of the Re-bpy moiety ($|S_D| = 0$). In the case of M = Cr^{III}, the $^4A_2$ ground state ($|S_A| = \frac{3}{2}$) creates a spin manifold in the reactant angular momentum space spanning $|S_R| = \frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$; this requires coupling to an excited state of the acceptor characterized by $|S_A| = \frac{1}{2}$, $\frac{3}{2}$, or $\frac{5}{2}$ in order to realize a spin-allowed pathway. Angular momentum conservation is clearly satisfied with the $^4T_2$ excited state of the Cr^{III} core ($|S_{A*}| = \frac{3}{2}$), as are thermodynamic considerations by virtue of the resonant condition that exists between the Re-bpy emission and the $^4A_2 \rightarrow {}^4T_2$ absorption. Thus, dipolar energy transfer can proceed through the commonality of $S = \frac{3}{2}$ states in both the reactants and products, and excited-state quenching of the ^{3}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 Co(pyacac)$_3$ core fundamentally alters the momentum conservation condition. Specifically, the phosphorescent nature of the $^3MLCT \rightarrow {}^1A_1$ emission requires coupling to an excited state of the Co^{III} having $|S_{A*}| = 1$, not $|S_{A*}| = 0$, which defines the $^1A_1 \rightarrow {}^1T_1$ 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 thermodynamically 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.

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Supporting Online Material

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Graphitic Tribological Layers in Metal-on-Metal Hip Replacements

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Arthritis is a leading cause of disability, and when nonoperative methods have failed, a prosthetic implant is a cost-effective and clinically successful treatment. Metal-on-metal replacements are an attractive implant technology, a lower-wear alternative to metal-on-polyethylene devices. Relatively little is known about how sliding occurs in these implants, except that proteins play a critical role and that there is a tribological layer on the metal surface. We report evidence for graphitic material in the tribological layer in metal-on-metal hip replacements retrieved from patients. As graphite is a solid lubricant, its presence helps to explain why these components exhibit low wear and suggests methods of improving their performance; simultaneously, this raises the issue of the physiological effects of graphitic wear debris.

Arthritis, or rheumatism, is the leading cause of disability, affecting an estimated 8.6 million people in the United States as of 2005 (*1*), with comparable estimates elsewhere. By 2030, the number of American adults aged 65 and older (the segment of the population with the highest prevalence of arthritis-related disability) will double to ~71 million (*1*). For individuals afflicted with end-stage arthritis of the hip, arthroplasty is the most cost-effective and clinically successful treatment. Currently, up to three total hip replacement procedures per 1000 inhabitants are performed in countries belonging to the Organisation for Economic Co-operation and Development (*2*); Germany leads with the largest number of replacements per capita, and the U.S. performs the most procedures overall. As of 2003, ~202,500 primary total hip replacements were performed annually in the U.S. By 2030, this number is expected to increase by more than 174% to ~572,000 hip replacements. Arthritis of the hip has an increasingly large public health impact in terms of morbidity, disability, and the cost of disability and treatment. To minimize the impact on the individual patient and society, it

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