Potential for Light-induced Separation of Critical Rare-Earth Elements

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ABSTRACT

Current methods for separations of critical rare earth elements (REEs) require multi-step, waste-generating procedures that lack the ability to selectively separate similarly sized ions, despite such an onerous process. REEs possess unique optoelectronic properties that are often exploited for photomagnetic or photoluminescent applications but could be harnessed to drive element selective separations. Recent work exploring photochemical reactions of REE complexes points to promise for investigating alternative separations using photoactive molecules and macromolecular frameworks, highlighting a possible pathway towards realizing practical REE separations to increase the sustainability and longevity of mining and recycling these elements.

Rare-Earth Element Criticality

The 17 **rare earth elements** (REEs, **See Glossary**), comprising the lanthanides (La–Lu), plus Sc and Y, have been designated by a number of governmental organizations in the U.S. and European Commission as **critical materials**,[1–3] due to their use in a variety of industrial sectors and prevalence in technologies that touch almost every aspect of our daily life. More specifically, in 2011 the U.S. Department of Energy has classified the elements Nd, Eu, Dy, Y, and Tb as critical in the short term,[1] a designation that still holds true today.[3] Despite their name, the REEs are more abundant than all the precious metals and similarly abundant to a number of major industrially utilized metals (Figure 1A).[4] The rarity, criticality, and associated cost arise due to their proclivity to exist as low concentration mixtures in REE-containing ores and the fact that chemical extraction and separation processes must overcome their similar chemical properties to yield high purities of the individual elements.[5] In addition, the vast majority of REE production occurs in China, adding further complexity to the global supply chain for these critical elements.

Separations Overview

The current state of the art for industrial REE separation and enrichment relies on a multi-step, counter-current solvent–solvent extraction process (Figure 1C). For a more comprehensive discussion of the research developments and practical implementation, including process improvements and current limitations, we direct the reader to a number of excellent reviews.[6,7] Briefly, this process utilizes reactive separation at the interface between an acidic aqueous solvent phase containing the RE mixture and a water-immiscible organic solvent phase containing ligand extractants. The REE extraction/separation relies on partition (or distribution) coefficients that reflect the small, but systematic, changes in the size-dependent Lewis acidity of the REEs (Figure 1B). Despite an extensive and vibrant global market for purified REEs and a wealth of minable rare earth-containing ores within the U.S., the existing purification process is time/resource intensive, producing huge quantities of hazardous waste, making it prohibitively expensive to mine, extract, and separate REEs currently in the U.S. As such, there is a substantial effort, supported by several federal research agencies including the U.S. Department of Energy, devoted to either improving the current separation techniques or developing new approaches that promise more selective and efficient separations of target REEs. In the last decade, several novel approaches have been developed that are based on tailoring the chemistry of the coordinating

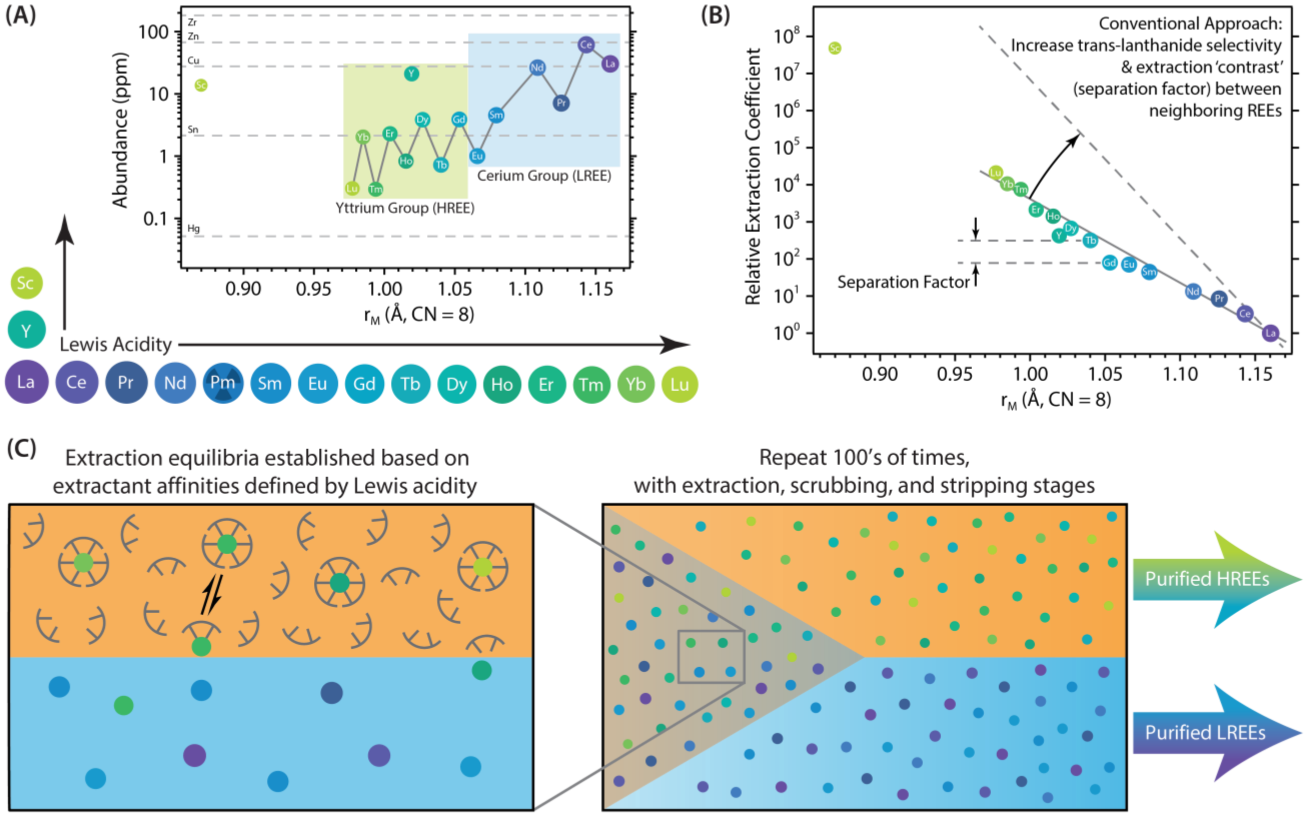

Figure 1. Rare-earth Element Criticality and the Conventional Extraction/Separation Process

(A) Classification of the REEs according to their position in the periodic table, illustrating the trend in Lewis acidity, and the upper crustal abundance of the REEs as a function of the REE ionic radius for a coordination number of 8, according to Ref. 5. (B) Illustration of the conventional approach to enhancing the relative extraction coefficient, which relies on modifying the extractant chemistry and composition to increase the slope of the trans-lanthanide selectivity to enhance separation factor 'contrast' between neighboring REEs, plotted against the REE ionic radius for a coordination number of 8. Panels (A) and (B) are adapted from Ref. 5 with permission from American Association for the Advancement of Science. (C) Cartoon of the solvent−solvent extraction process currently employed for REE extraction/separation via selective partitioning of the REEs at the interface between acidic aqueous (blue) and organic (orange) solvent phases.

ligands to exert thermodynamic or kinetic control of the separation process and, more recently, on exploiting the magnetic properties of certain rare earth metal ions to amplify the thermodynamic/kinetic separation, approaches that were summarized by the Schelter Group at University of Pennsylvania in an Accounts of Chemical Research article in 2022.[8]

While we detail the history of light-induced separations of REEs in this work, the authors note that there are currently only a few case studies in the literature that demonstrate the viability of this approach. Here, we emphasize the potential, opportunities, and challenges related to an emerging concept that seeks to exploit the unique optical/electronic properties associated with the electronic transitions of *f*-electron states of the rare earth metal ions (Figure 2). We focus on the use of photoactive chromophores appended to ligands or embedded into scaffolds/frameworks to exploit either (i) rare earth-specific perturbation of **photochemical** reactions or geometrical changes in **photoswitchable** chromophores to drive changes in REE solubility and/or **phase partitioning** (Figure 2D) or (ii) geometrical changes in systems bearing photoswitchable chromophores to influence binding/release of REEs. We discuss a variety of molecular platforms from light-harvesting antenna ligands to macromolecular frameworks, which are currently used for separations of small molecules from CO_2 to propylene.[9,10] Many of the approaches referenced here incorporate REEs, but for applications other than separations, including enhancement of photoluminescent or photomagnetic properties. The understanding gleaned from these studies regarding REE influence on **photophysical** properties in these different molecular complexes and scaffolds paves a path forward for light-induced separations.

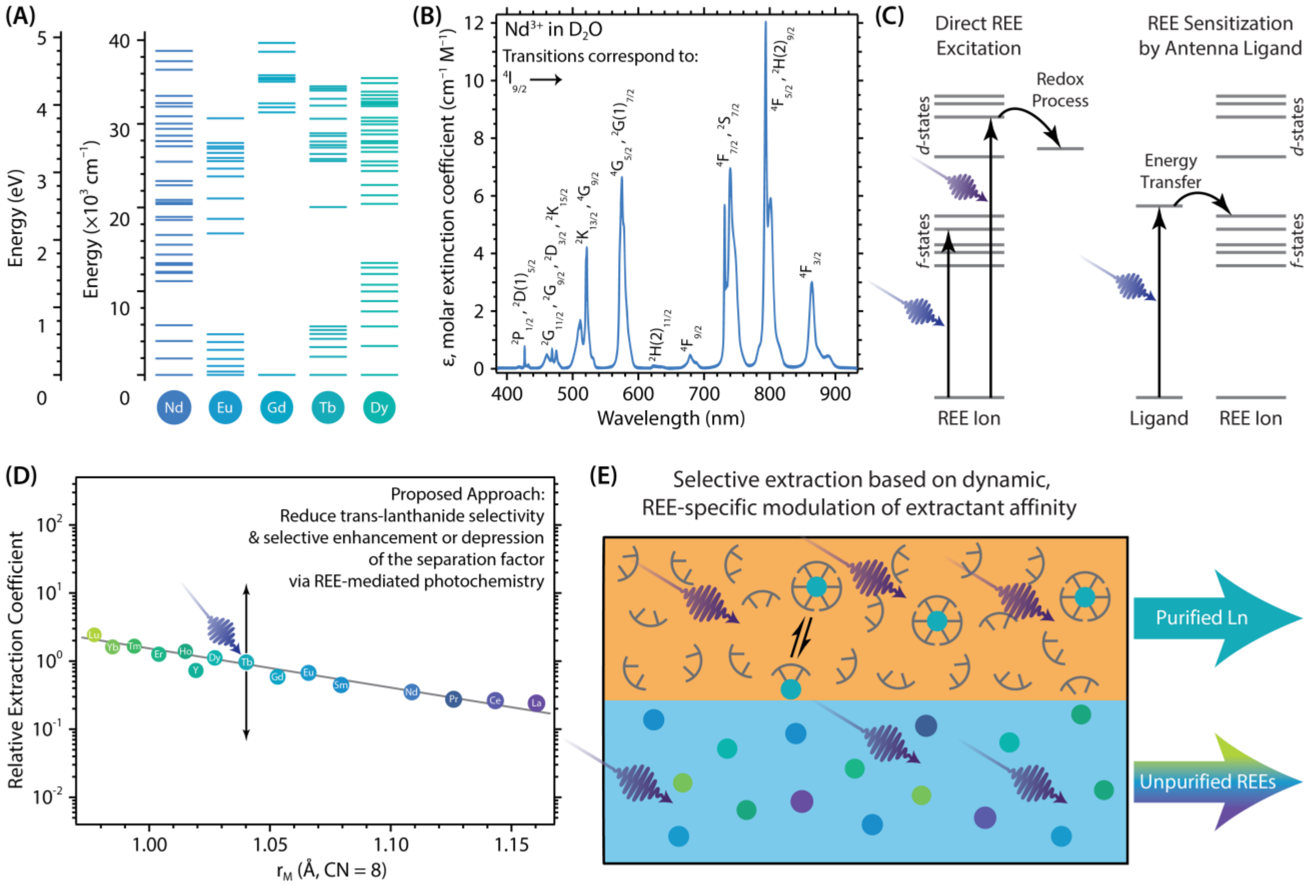

Figure 2. Exploiting the Unique Optical/Electronic Properties of Rare-earth Elements for Light-driven Separation Processes

(A) Schematic showing the energy levels associated with *f* electrons for the trivalent REE ions of Nd, Eu, Tb, and Dy that have been designated as critical in the short term, along with Gd for reference, illustrating the distinct differences in the excited state manifolds. (B) Representative absorbance spectrum for a Nd^{3+} complex in D$_2$O, illustrating the very weak electronic transitions of the trivalent REE ions. Adapted from Ref. 13 with permission from Royal Society of Chemistry. (C) Schematic of two alternate photophysical schemes for generation of excited states in REE metal ions by (left) direct excitation or (right) sensitization of the REE via energy transfer after light harvesting by an antenna ligand. Controlling the dynamics and interplay of the ligand and REE excited states could mediate reactions to kinetically alter the solubility and/or phase partitioning of REE complexes. (D) Illustration of the proposed approach for light-induced, dynamic modification of the separation factor of a specific REE mediated by the unique REE excited states, plotted against the REE ionic radius for a coordination number of 8. (E) Cartoon illustrating the use of light for selective extraction of single REEs via exploitation of the different photophysical kinetics to impart dynamic control over the affinity of the extractant for specific REE metal ions.

Photochemistry Driven by Direct Excitation of REE Metal Ions

While the light-driven separation of REEs was originally explored almost half a century ago,[11] the concept is still relatively underexplored and little progress has been made toward practical separation processes. Initial efforts focused on the use of narrow bandwidth laser excitation for direct, selective excitation of the distinct electronic transitions of the (trivalent) rare earth ions to drive photochemical redox processes primarily centered on the metal ion.[11,12] However, the photochemical redox processes required for separation were not observable by single photon excitation of the ***f-f* transitions**, likely due to the weak **oscillator strength** that originates from the "forbidden" nature (according to the Laporte parity rule) of the transitions (Figure 2B),[13] the need to select redox processes with sufficient thermodynamic driving force to be sensitized by *f*-electron states, and the strong shielding of the valence *f* electrons. Instead an alternative approach utilizing ultraviolet or multiphoton excitation of charge transfer or ***f-d* transitions** has been employed to access photochemical redox active states.[14] These preliminary light-driven efforts were most effective for separating Eu and Ce, since they possess quite stable 2+ and 4+ oxidation states, respectively. For example, photochemical reduction of Eu(III) with high energy photons ($\lambda \leq 254$ nm) generates stable Eu(II) that precipitates out of a Eu/Y mixture with the addition of sulfate to generate $EuSO_4$ with high purity (96%).[15] Similarly, Ce(III) can be photo-oxidized with UV photons to Ce(IV) and precipitated out of solution with iodide with high separation factors over a series of Lanthanide ions.[16] In contrast, the other REEs possess extremely stable trivalent ions and photochemical redox via direct excitation of the ion is insufficient to be practical for effective separations.[15–20] Efforts are ongoing to understand and improve this process for Eu and Ce, and research aimed at exerting stabilization of oxidation states other than 3+ for other lanthanides points to opportunities to extend the approach more broadly across the REEs. More recently, this approach was extended to the actinides, where resonance-enhanced multiphoton charge transfer was demonstrated in trivalent americium.[21]

To circumvent the inaccessibility or instability of non-trivalent REE metal ions via photochemical redox processes, researchers have explored a parallel approach aimed at sensitized photodissociation of coordinated ligands after direct excitation of an *f-f* transition. This has been demonstrated for Pr(III), Eu(III), Ho(III), and Tb(III), where an irreversible reaction due to the destruction of the photodissociated ligand(s) is followed by replacement by coordinating solvent ligand(s), though this approach resulted in low yields.[12,22] Selective excitation of electronic transitions with mixed metal ion-ligand character has been employed in separations of transition metal ions (Ru(II) and Fe(II)), where a photochemical ligand transformation alters the charge on the complex allowing for chromatographic separation.[23] It remains to be seen whether such an approach can be universally applied to metal-ligand charge transfer states in REE **coordination complexes**.

Overall, the high energy or multiple photons required to directly excite metal centered *f-f* transitions, coupled to their low oscillator strength, make realizing practical separations difficult. Additionally, selective excitation of the metal center or metal-ligand states would also require use of many monochromatic light sources (e.g., lasers or narrowband light-emitting diodes) to enable separation of a variety of REEs. An alternative strategy we explore below utilizes the unique properties of the metal centered excited state transitions combined with the light-harvesting properties of organic ligands without the need for selective excitation.

Photochemistry Driven by Sensitized Excitation via Light-harvesting Antenna Ligands

In contrast to the previous studies, recent work has explored exploitation of the strong absorption by light-harvesting antenna ligands to overcome weak absorption of *f-f* electronic transitions associated with the REE metal ions,[24] including **chromophores** with strong two-photon absorption cross-sections.[25] This approach introduces a challenge regarding REE-selective reactivity that depends on the relative kinetics and thermodynamics of excited state processes and is predicated on differences in interactions between ligand and REE metal ion excited states for the individual REEs. We identify studies that demonstrate differences in photophysics and photochemical reactivity of ligands in coordination complexes that depend on the electronic properties of the REE metal ion and point to the validity of the approach for REE separations.

In 2023, the idea of photochemically-driven ligand reactivity and substitution was revisited by Ruoff, Gish and coworkers (Figure 3).[26] Utilizing a photoinduced oxygen atom transfer and ligand replacement, substantially different photoreactivity was observed between two similarly sized rare earths, Y(III) and Dy(III), which exhibit comparable ground state chemical reactivity. Here, differences in the energetic overlap between the coordinated ligands and the metal center were exploited to control photoreactivity under illumination. In the Y(III) complex, the absence of an accessible *f*-electron manifold of states means that photon absorption by the β-diketonate (1,1,1,5,5,5-hexafluoroacetylacetonate, hfac) **antenna ligand** is followed by energy transfer to a photochemically active *N*-methylmorpholine-*N*-oxide (NMMO) that undergoes oxygen atom transfer (OAT) with a triphenylphosphine oxygen atom acceptor in solution. The triphenylphosphine oxide (TPPO) formed by the OAT reaction subsequently replaces the NMMO moiety in the Y(III) coordination sphere. In contrast, the *f-f* transitions in the Dy(III) complex were accessible to the excited state manifold of the ligands, making rapid and efficient energy transfer possible to the REE metal ion (Figure 3B). This effectively slowed the photochemical reaction for Dy(III) compared to Y(III) (Figure 3C). Unlike the earlier attempts using direct excitation, this strategy does not require the use of high-intensity excitation (i.e., by a laser) and could potentially be driven by sunlight, albeit in the ultraviolet portion of the spectrum. Although the lability of the NMMO ligands employed in this study prevented demonstration of a practical separation due to ligand scrambling in mixtures of the Y(III) and Dy(III) complexes, this study sets the stage for practical light-driven separations of REEs.

Complexes of La(III) and Ce(IV), f^0, and Ce(III), f^1, with a similar ligand, 2-thenoyltrifluoroacetone (TTA), exhibit a variety of excited state transitions, including ligand-to-metal charge transfer (LMCT), ligand localized (LL) states, and an unprecedented visible metal-to-ligand charge transfer (MLCT) state in Ce(III) (Figure 3D).[27] La(III) only exhibits ligand centered transitions, while the ligand and metal interact in the Ce complexes, pointing to potential differences in photochemical reactivity. Both studies above emphasize the role of triplet excited states in the photophysical pathways, with intersystem crossing rates dependent on the metal center and long lifetimes suitable for exploiting these spin-based properties to drive photochemical reactions for REE separations.

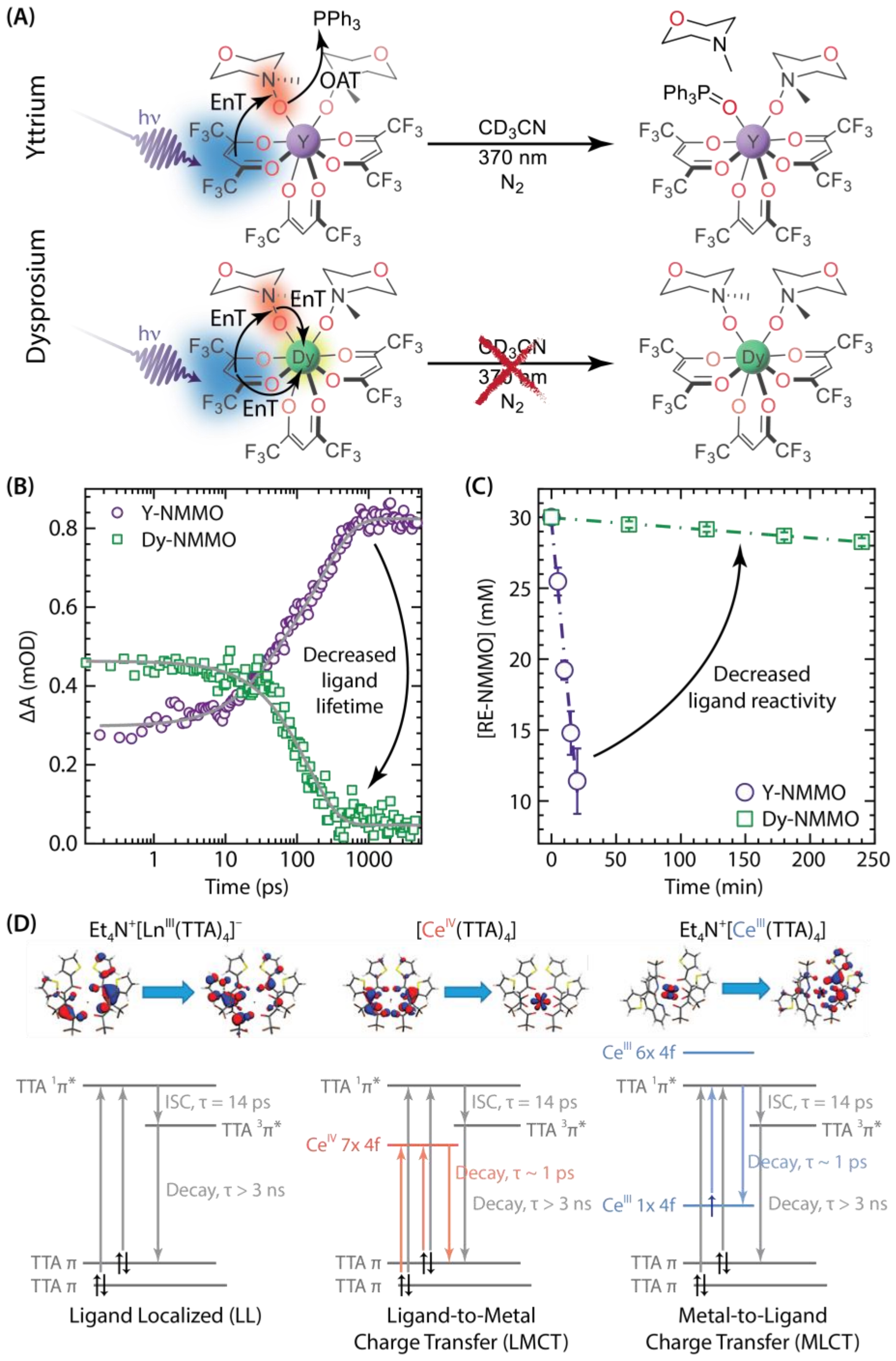

Figure 3. Photochemical Reactivity Mediated by Rare-earth Electronic States

(A) Cartoon illustrating the differences in the photophysical and photochemical pathways for Y and Dy complexes with 1,1,1,5,5,5-hexafluoroacetylacetonate (hfac) and *N*-methylmorpholine-*N*-oxide (NMMO) that result in dramatic differences in the (B) NMMO ligand excited state lifetimes and (C) oxygen atom transfer reactivity after photon absorption by the hfac ligand(s). Adapted with permission from Ref. 26. Copyright 2023 American Chemical Society. (D) Representative natural transition orbitals and the corresponding Jablonski diagrams of the electronic states for La(III), Ce(IV), and Ce(III), complexes with 2-thenoyltrifluoroacetone (TTA), illustrating ligand localized states for the La(III) complex and contributions from mixed metal ion-ligand states for the Ce(IV) and (Ce(III) complexes. Adapted with permission from Ref. 27. Copyright 2023 American Chemical Society.

Candidate Light-Driven Photochemical Reactions

Several candidate chromophores exhibit interesting photophysical and photochemical properties upon photoexcitation that could be manipulated for REE-selective separations (Figure 4A). The spectroscopic and theoretical studies described above point to the importance of ligand triplet excited states to mediate the reaction, which is unsurprising given the proximity of the chromophore to the heavy lanthanide ions. This observation suggests that photochemical reactions known to proceed via triplet excited states, such as sensitization of reactive singlet oxygen ($^1O_2$) or various photocycloadditions (e.g., [2+2] or [4+4], see Figure 4B), could offer a route to selectively modify the coordination sphere surrounding the REE metal ion for separations.

The generation of $^1O_2$ by lanthanide ions has been studied for in-vivo therapeutic use; quantum yields of $^1O_2$ generation comparing several REEs indicate that Gd(III) produced almost 6 times the amount of $^1O_2$.[28,29] This observation touts the promise of this route if complexes are designed with separations in mind. The formation of $^1O_2$ could result in the production of endo-peroxides[30] or related oxygenates[31] in the ligand shell of triplet-sustaining complexes, which may cleave or shed binding moieties. These modifications of the ligand sphere, where the yield/rate of reaction depends on REE-specific excited state dynamics, would result in complexes with altered solvation properties, providing a means to separate complexes based on their different solubility.

The photocycloaddition reactions could involve two ligand chromophores in the coordination sphere (e.g., dimerization of anthracene via a [4+4] cycloaddition) or one ligand chromophore with an exogenous reactant (e.g., [2+2] cycloaddition of two alkenes).[32–34] The cyclized products for ligand-ligand reactions could exhibit a strain-induced increase in ligand lability, leading to instability of REE complexes where the ligands undergo the reaction (*i.e.*, where the RE *f*-electron states cannot deactivate the ligand excited state) that reduces the solubility and engenders separability. For exogenous light-induced cycloadditions, moieties containing the exogenous olefinic bonds could remain free in solution and must therefore incorporate substituents that alter the solubility of the complex after reaction in solvents used in the separation process. In contrast, the olefin could be incorporated into porous supports (such as the supramolecular assemblies or framework materials described below) to immobilize reactive species at sites within the pore structure.[10,35]

Exploiting the changes in the electrochemical redox properties exhibited by the different photostationary states of some of the photoswitchable chromophores described below can drive photoelectrochemical reactions that alter the coordination sphere and solubility of the REE complexes.[8,36] This strategy could be explored as a path to accessing excited-state redox processes associated with the RE metal ion that are typically inaccessible in the ground state. Photoactive ligands have also been used for selective sensitization of RE metal ions or changes in metal oxidation state via coupling with *d*-orbitals through metal/ligand charge (redox) processes.[37–40] Harnessing conformer-dependent differences in photochemical reactivity could enable targeted reactions affecting solubility and/or phase partitioning.

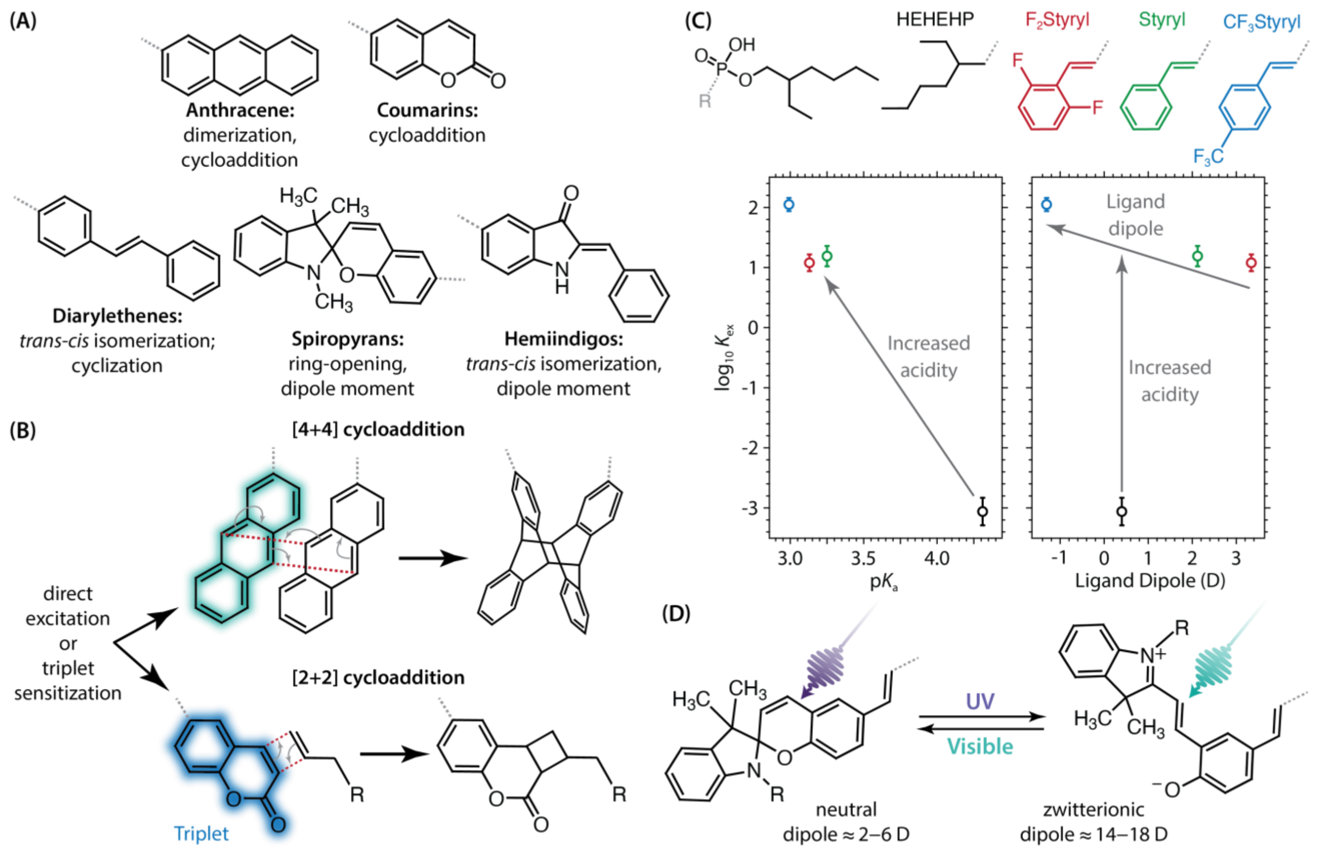

Figure 4. Candidate Chromophores for Photochemical and Photophysical Reactions

(A) Chemical structures of chromophores known to undergo photochemical reactions or photoisomerization. (B) Schematic illustrating representative cycloaddition reactions that can be induced via either (i) direct excitation and intersystem crossing to form the chromophore triplet excited state or (ii) sensitization by a chromophore, either part of the metal ion coordination sphere or exogenous to the complex, that produces triplets with high yield. (C) Data illustrating the importance of ligand acidity and dipole on the extraction strength, K_{ex}, of aryl-vinyl phosphonic acid esters, via chemical modification of the styryl unit. Adapted with permission from Ref. 61. Copyright 2023 American Chemical Society. (D) Schematic illustrating the photoisomerization of a spiropyran derivative to its zwitterionic merocyanine form, indicating the large associated increase in the molecular dipole.

Opportunities to Exploit Photoswitchable Chromophores

The next steps in the development of light-driven separation for REEs can be found in adapting existing strategies in dark extractions or adjacent fields related to light-driven switchable materials. A common thread that connects these approaches is the use of, or potential to use, photoswitchable molecules (Figure 4A) where photoswitching refers to light-induced changes in structural geometry of the photostationary states, including ring opening/closing (Figure 4D), or *trans*-to-*cis* (*E*-to-*Z*) isomerization, leading to changes in physicochemical and optical/electronic properties. Several excellent review/perspective articles have been published that cover the interesting properties and myriad potential applications for a variety of photoswitchable molecular chromophores (e.g., azobenzene, stilbene, hemiindigo, dithienylethenes, spiropyran, and more),[41–45] including dynamic binding and release of small molecules[9,46,47] and ions.[48–50] This section will cover a high level understanding of the switching mechanisms and properties of photoswitchable molecules and how they could be adapted for REE separations.

Photon-driven chemical rearrangement of molecular chromophores could be used to dynamically tune the coordination environment and solubility of REE metal ions via manipulation of either (i) the binding geometry/steric effects that destabilize the coordination environment or (ii) the excited-state dipole of a ligand extractant to alter interactions that depend on solvent polarity. It is likely that both effects will play some role in differences between the physicochemical properties of complexes bearing ligands containing the chromophores in their different photostationary states. For instance, *trans*-to-*cis* (*E*-to-*Z*) **photoisomerization** of azobenzene,[43,44,51–53] hemiindigo,[54] and diarylethenes[42,55] (e.g., stilbene,[56,57] dithienylethene,[58–60] etc) derivatives and photoinduced ring closing/opening of the *cis* (*Z*) isomer of diarylethenes results in dramatic differences in the shape of the molecule in the two **photostationary states**. Depending on the precise nature of the binding motif of ligands that incorporate these chromophores, the photoswitching could influence the binding configuration of the ligand to the metal ion (i.e., mono- vs. multi-dentate) or alter steric and non-covalent interactions between neighboring ligands, leading to dramatic changes in the stability of the coordination sphere that could be exploited to drive changes in the solubility of REE complexes in solvent−solvent extraction processes.

Recently, Kuvayskaya *et al*.[61] demonstrated a new class of aryl-vinyl phosphonic acid esters (aryl-VPAs), whereby the nature and position of moieties added to the phenyl ring of the styryl group (which affects the Hammett parameter) determines the acidity and dipole of the molecule, which in turn affects the extraction strength for Eu(III) from aqueous acidic media (Figure 4C). The increased acidity enhances the extraction strength compared to best-in-class extracting ligands such as 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEHEHP). However, the observation that the ground state molecular dipole of the aryl-VPAs ultimately determines the trend in their extraction strength points to photoinduced modification of molecular dipoles via ligand extractants bearing chemically tailored photoswitchable chromophores as a potential strategy for dynamic control of REE extraction/separation. The ring-opening photoisomerization of neutral spiropyran derivatives to generate the zwitterionic merocyanine form is associated with a large increase in the molecular dipole, that can be stabilized by polar solvents. In contrast, other chromophores that exhibit large geometrical changes during photoisomerization without large dipole modification could be functionalized with strongly electron donating or withdrawing substituents that amplify the difference between the dipoles of their photostationary states and alter their solubility in polar solvents. Since REE extractions are performed across a liquid−liquid interface between polar (typically acidic aqueous) and non-polar (typically aliphatic organic) solvents, large photoinduced changes in the dipole points to tailored photoswitchable chromophores as a potential route to selective separation of target REE metal ions due to changes in solubility and partition coefficients in polar/non-polar solvents.

In addition to the large dipole moment change, merocyanine also exhibits chelation of metal ions, including REEs such as Gd(III) and Eu(III) that are reversibly expelled during back conversion to spiropyran.[49,62] Similar behavior has been demonstrated with Y(III) and Dy(III).[59,63,64] Neither of these studies focused on REE separations, but rather in vivo metal chelation and photomagnetism of REEs, respectively; however, the path towards designing functional spiropyran/merocyanine materials is laid out by these previous studies.

Photoswitches in Frameworks and Macromolecular Scaffolds

The ability to construct tailored, highly selective, synthetic binding pockets for REE extractions/separations can perhaps take some inspiration from the pioneering discovery of biological proteins (e.g., lanmodulin, LanM) that exhibit binding pockets with a 100 million-fold greater selectivity for trivalent REE ions over divalent calcium[65,66] and have been used to recover and separate REEs.[67–69] While biologically-inspired protein systems hold enormous promise for an understanding of the chemical specificity of REE binding and even practical separations, it is unclear whether they could be easily modified to exert dynamic control over the selectivity of the binding motifs in a manner similar to that described in the previous sections. In contrast, macromolecular and supramolecular scaffolds, including extended metal- or covalent-organic frameworks (MOFs/COFs), have emerged as a compelling platform for the capture, storage, and release of small molecules and ions, since they are amenable to significant tunability of the size, shape, and local dielectric properties of their pore structure. Lanthanides are already a common addition to macrocycles and MOFs within the framework as well as incorporation into pores or cavities, although they are primarily employed to enhance photoluminescent or photomagnetic properties.[40,70–74]

Additionally, several photoswitches have already been incorporated into such systems,[41–43,45] suggesting that dynamic control of the properties of the pores is a viable strategy for REE separations that exploit some of the photoinduced processes described above. These supramolecular assemblies and framework materials often employ photoswitches to control properties like cavity size and polarization, with capture, storage, and release of gases (e.g., CO_2 or H_2) a high value target application.[10,75–77] Despite being tethered into a larger molecular assembly or extended framework, azobenzene has still been demonstrated to undergo a reversible *trans*-to-*cis* photoisomerization.[48,51,53,75,77–80] For instance, Falkenburg, *et. al* synthesized a 12-membered macromolecular ring containing azobenzene with near unity conversion between the photostationary states under white light illumination,[80] and MOFs and COFs functionalized with azobenzene exhibit photoinduced changes in pore size that have been exploited to encapsulate metallofullerenes with REEs[78] and small organic molecules,[9] with light-controlled release upon photoisomerization. A recent study from the Feringa group[81] found that azobenzene in the backbone of a MOF (DUT-163) led to either full photoconversion to the *trans*-isomer or a light-induced buckling dependent on the orientation of the azobenzene moiety within the same framework. This study points to some subtleties associated with the photoisomerization processes within frameworks and highlights the need for further studies to elucidate mechanistic insight that will inform the

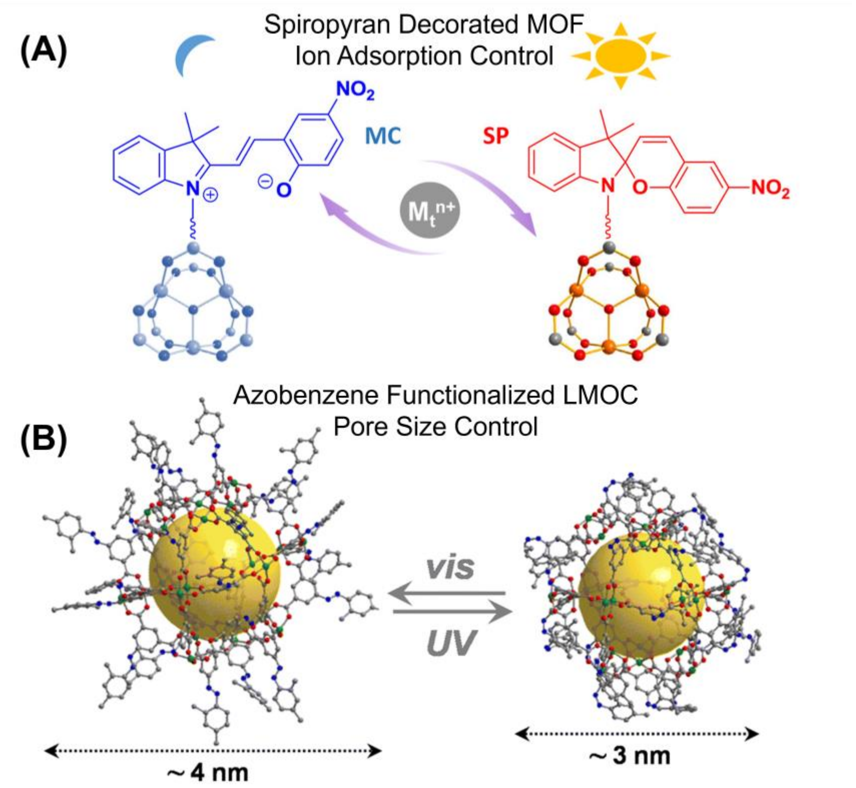

Figure 5. Photoswitchable Molecules Incorporated into Supramolecular Assemblies and Frameworks.
(A) Spiropyran-decorated metal-organic framework (MOF). A photoinduced ring-opening to merocyanine provides a site for ion adsorption. Adapted from Ref. 82 with permission. Copyright 2023 American Chemical Society. (B) Azobenzene-functionalized light-switchable metal-organic cage (LMOC). Photoisomerization controls the pore size for propylene ad-/de-sorption. Adapted from Ref. 10 with permission from the Chinese Chemical Society (CCS), Peking University (PKU), and the Royal Society of Chemistry.

intelligent development of photoswitchable porous supramolecular assemblies and extended frameworks for dynamic binding and separation processes. Size selective ion uptake of monovalent and divalent salts has been observed in spiropyran-functionalized MOFs[82] (Figure 5A) suggesting the photoinduced changes are enough to accommodate small differences in ion size. Figure 5B shows a light-switchable metal-organic cage (LMOC) composed of azobenzene units, where a light-induced conformation change from the *trans*-isomer to the *cis*-isomer reduces the size of the pore. This work studied CO_2 adsorption and desorption as a function of photoexcitation, but adaptation of this system for REE separations could be imagined.[10]

Overall, light-responsive macromolecular scaffolds and frameworks are successful in adsorbing small molecules in a variety of conditions, including separation of CO_2. Capture of REE ions has also been demonstrated in similar systems[83] but often with the purpose of enhancing emissive[84] or magnetic properties.[85] Lanthanide incorporation into MOFs/COFs[86,87] suggest that scaffolds could be designed or adapted that are capable of dynamically binding specific REEs under photoexcitation to harness light to drive separations.

Concluding Remarks

Adapting these strategies for REE separations will come with challenges. Size selectivity remains the top challenge in all separation strategies. For example, light-driven changes in pore size in macromolecules or frameworks may be a viable strategy, but how significant do the changes in pore size need to be to successfully separate similarly sized REEs. Ideally, the goal of driving separations with light must be more sustainable and less wasteful than current solvent extraction methods. As such, ligand systems or macromolecular frameworks to successfully harness photoinduced separations must not be expensive or use rare metals, and must be robust enough to withstand the harsh environments typically required for REE extraction and separation. To overcome these challenges, the inherent properties of the REEs need to be at the forefront of design considerations.

The ability to exploit the photochemical and photoisomerization processes described above to effect selective separation of critical REEs will ultimately depend on the thermodynamics and kinetics of the relevant photophysical and photochemical processes, i.e., relative energies of the various excited states, the rates of transitions between them, and the ability to exert influence of these depending on the identity of the REE metal ion via their unique manifold of *f*-electron excited states.

Developing practical light-driven applications of REE separations will require significant strides in understanding fundamental photophysical behavior of rare earths and ligand/framework interactions (see Outstanding Questions). A significant focus of REE photophysical studies in the last decades has been enhancement or detection of luminescent or photomagnetic properties.[40,70–72,88–92] Demonstrations of light-driven separations are often limited to only a few elements, such as Eu(III), Y(III) and Dy(III)[15,17,19,26] and lack systematic studies across the entire series of REEs. To push this field forward, there is a need to understand mechanisms, including the effect of REE identity on reaction kinetics and thermodynamics. A combination of theory and spectroscopy must be employed to connect photophysical dynamics to photochemistry, which will, in turn, inform the design of the next generation of ligands/extractants that employ photoactive chromophores to facilitate selective separations (bottom right of Figure 6). The knowledge gained from other applications of light absorbers involving REEs can inform theoretical studies pairing metal ions with well-known ligands. Using transient spectroscopic techniques that access time scales below 1 ms, and even ultrafast techniques that access dynamics on time scales <1 ns, can be critical in understanding the rate limiting step of a photochemical reaction, especially when tied to characterization of the photochemical reactions (Figure 6). Techniques that are sensitized to dipole moments and spin states inform interactions between REEs and ligands or frameworks after photoexcitation can be observed in real time highlighting successes and pitfalls. Design principles for light-driven separations can be determined with the appropriate experimental design and understanding of metal-centered excited states.

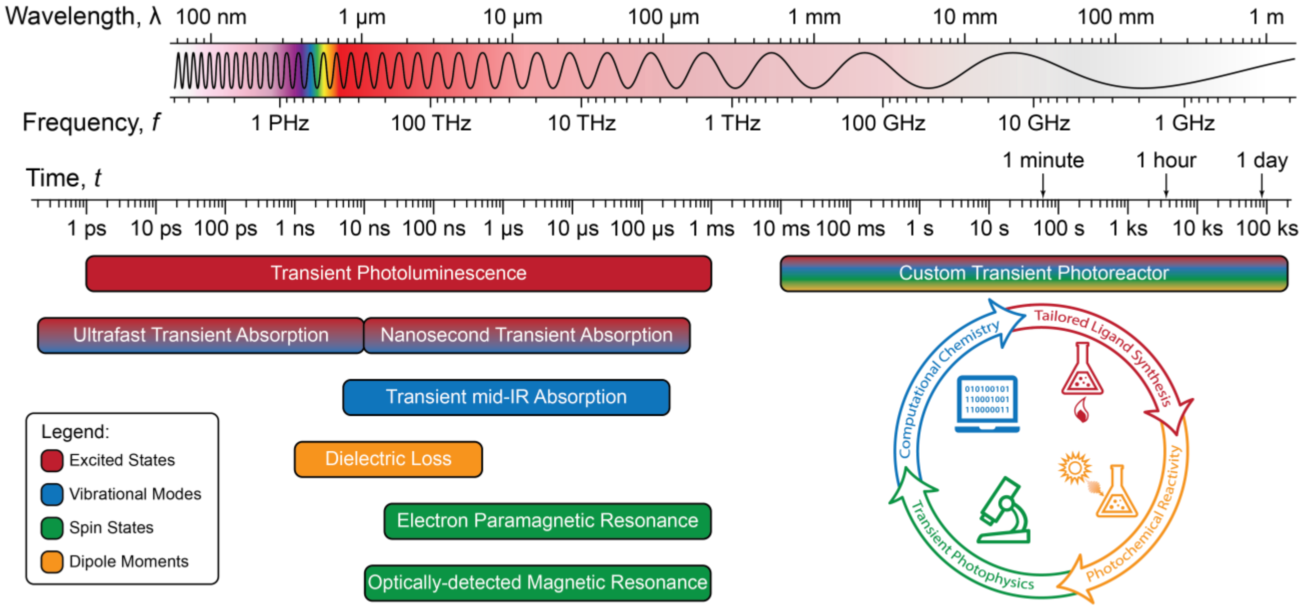

Figure 6. Multidisciplinary Approach to Fundamental-to-Applied Research of REE Separations

(A) The feedback loop that informs the design and synthesis of next-generation ligands for REE extractions/separations, via experimental evaluation of practical photochemical reactivity, transient spectroscopic studies of the excited-state photophysics, and computational chemistry to identify chemical descriptors of structure-function relationships. (B) The broad portion of the electromagnetic spectrum and the time scales available for transient spectroscopic studies aimed at understanding the role of dynamics associated with electronic excited states, vibrational/phonon modes, spin states, and dipole moments on the photochemical reactivity.

The industrial adoption of light-driven separation of REEs, and indeed any photochemical separation process, must overcome the trade-off between being able to conduct the separations at scales large enough to ensure that the process is efficient/cost effective and the constraint that excitation with photons is limited by the fundamentals of light absorption (i.e., the Beer-Lambert

Law). The partially forbidden nature of the *f*-*f* transitions loosens this restriction slightly for approaches based on direct excitation of the REE metal ion, and there may be opportunities to exploit non-linear (i.e., two-photon) excitation processes, although these can also be quite weak. One alternative could be to use flow techniques based on micro-reactors, where the path length of the reaction mixture flowing through the excitation volume is sufficiently small to allow for effective excitation. Such micro-reactors have been employed in the synthesis of high-quality optoelectronic polymers with excellent control over the size distribution,[93] for the autonomous synthesis of metal chalcogenide and metal-halide perovskite nanocrystals,[94,95] and even for optically-controlled separation of immiscible liquids.[96] These studies often employ optical spectroscopy techniques to probe the physicochemical properties of the analyte and provide continuous feedback to optimize the processing, suggesting their applicability to both drive and monitor the photochemical reactivity and separation of critical REEs.

Finally, it will be important to consider technoeconomic factors that will dictate the viability of the process for industrial light-driven REE separations. For instance, separation processes relying on direct excitation of the REE metal ion would likely require expensive single-wavelength lasers to drive the weak electronic transitions with sufficient excitation density to achieve the desired photochemical reaction. Such laser-based excitation sources also typically consume large amounts of energy and require careful consideration of associated safety hazards and maintenance requirements. In contrast, the use of strongly absorbing antenna ligands with tuned electronic transition energies, with the photochemical reactivity then mediated by tailored electronic interactions with specific REE metal ions, opens the possibility of using broadband, incoherent excitation sources, and could conceivably even exploit ever-abundant sunlight, to drive photochemical separations, potentially reducing the associated energy consumption and cost. A detailed technoeconomic analysis is beyond the scope of this article but will need to consider factors such as (i) the nature of the light source and the photon flux/dose required to drive the photochemical reactions; (ii) whether the light-driven separation can replace, or must be integrated with, conventional approaches; and (iii) the social, economic, and environmental impacts[97,98] of the extractants and separation processes.

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Highlights

Sustainable separation of Rare Earth Elements (REEs) comprised of the lanthanides (La-Lu), and Sc and Y is crucial for the continued supply of these critical materials used in many ubiquitous technologies.

Light-driven REE separations promise elemental selectivity by exploiting unique optoelectronic properties, such as f-f transitions; however, direct excitation of metal-centered states is difficult due to weak absorptions.

Light-harvesting antenna ligands or frameworks have been used in similar applications for CO2, small molecule, and ion uptake, often including photoswitchable molecules that can alter properties, such as, structure, redox properties, and dipole moments.

The principles of light-driven separations of REEs have been demonstrated, though a practical separation has not yet been realized. Design principles from other separations provide a path forward.

Outstanding Questions

How can the unique optoelectronic properties associated with the *f*-electrons of similarly sized REE ions be exploited to interact with effective light absorbers for processes other than enhanced luminescence?

How can the thermodynamics and kinetics of the relevant excited state processes in photochemical REE complexes be controlled to facilitate tailored chemical reactivity toward manipulating the solubility and establishing separability?

Can the *d*-orbitals of REE ions be effectively accessed via photochemical pathways to make photoredox-based separations facile?

How can the pore size in supramolecular assemblies and frameworks be tuned dynamically and with sufficient spatial fidelity to promote size selective adsorption/binding of specific REE ions?

Can the photomagnetic properties of REEs be exploited to tune the rates of photochemical reactions or drive separations using magnetic fields?

How can we achieve selectivity while using earth-abundant, easy to synthesize materials?

Glossary

Rare Earth Element (REE): One of 17 elements comprising the lanthanides (La–Lu), plus Sc and Y that are designated as Critical Materials by a number of governmental organizations worldwide

Critical Material: Resources identified by the U.S. Government as vital components to energy technologies, economic and national security, and the manufacture of key products.

Phase Partitioning: Equilibrium concentrations of species that separate across an interface between two immiscible phases (e.g. solvents).

Electronic Transition: when electrons in a molecule are excited from one energy level to a higher energy level. These transitions determine the color of a molecule and provide information on its structure.

***f-f* transition:** Electronic transition that is formally Laporte-parity forbidden and gives rise to sharp, narrow absorption bands with weak intensity

***f-d* transition:** Electronic transition that is typically broad and intense and can be excited with multiple photons to access photochemical redox active states

Oscillator Strength: Dimensionless quantity that describes the degree to which an electronic transition is allowed and is proportional to the square of the transition dipole moment. Allowed transitions have a large oscillator strength while forbidden transitions have a low oscillator strength.

Chromophore: A group of atoms that absorb visible light of a specific frequency and gives a molecule its color.

Antenna Ligand: A molecule attached to a metal atom that increases the oscillator strength and, therefore, allowed transitions of the complex.

Coordination Complex: A chemical compound with a central atom, in this case a metal atom that is bound to a variety of molecules (ligands).

Photochemistry: Light-induced chemical transformations driven by excited state processes.

Photophysics: Light-induced dynamics including absorption, emission, and transfer of energy or electrons without a chemical reaction.

Photoisomerization: The light-induced conversion of one isomer to another in a molecule.

Photoswitch: A molecule that exhibits light-induced changes in structural geometry, including ring opening/closing, or trans-to-cis (E-to-Z) isomerization.

Photostationary State: A metastable configuration related to the specific isomer generated during photoisomerization.