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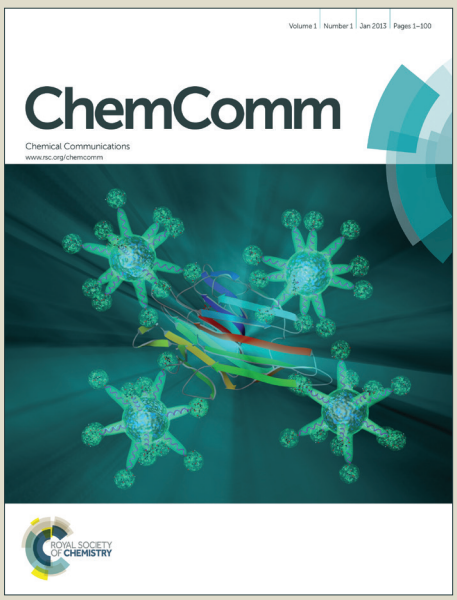

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Exploiting lanthanide luminescence in supramolecular assemblies

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Lanthanide ions, due to their unique photo-physical characteristics, have attracted considerable attention in recent years. Their long lifetimes, sharp, well-defined emission bands, and designable environmental sensitivity make them ideal for integration into switchable supramolecular assemblies where emission can report on local conformation and/or coupled energy levels (redox state). The immobilisation of lanthanide containing constructs on interfaces facilitates device integration, the fabrication of advanced sensory and molecular electronic platforms and presents a means by which conformational dynamics within molecular assemblies can be analysed. In this feature article we discuss the current and potential applications for lanthanide luminescence in supramolecular, switchable and surface bound architectures.

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Introduction

The unique photo-physical characteristics of lanthanides have stimulated significant interest in their application.[1-3] Their characteristic sharp emission bands and long lifetimes have been applied within a number of technologies, most particularly those associated with novel display and organic light emitting diode formats.[4-7] In addition, the emergence of complex, carefully designed, molecular architectures that can function as molecular switches[8, 9], molecular machines[10-13], data storage systems[14] and advanced transduction mechanisms in sensing platforms[15, 16] has opened a new frontier for the luminescent lanthanide systems. The incorporation of emitting species into such architectures offers a potent means of associating optical output with triggered conformational, coordinative, or electronic change.[17-19] Lanthanide complexes are especially attractive in this context because the lanthanide-centred luminescence spectrum can be readily separated from background fluorescence and scatter by using time-gating techniques and, in addition, is sensitively dependent on both coordination environment and interactions with local sensitisers.[3] Many of the platforms which have been perceived and developed require surface immobilisation in order to achieve device integration[10], yet surprisingly little is known about lanthanide emission characteristics at interfaces. In this feature article we discuss the reported and potential exploitation of lanthanide luminescence in solution, and surface bound, switchable systems and supramolecular assemblies.

Properties of Lanthanide Ions

Coordination Properties

Lanthanides, when complexed with organic ligands, almost exclusively exist in the Ln^{3+} oxidation state and behave as "hard" acids, with a binding preference of O > N > S. The valence 4f electrons do not predominantly preside in the outer region of the ions, and hence the resulting complexes are ionic in nature, exhibiting increased kinetic liability in comparison to transition metal complexes and preferentially binding to anionic species. The metal centre imposes little in the way of geometry (coordination numbers, spanning three to twelve, being determined by ionic radius and steric constraints arising from inter-ligand repulsions).[20]

Photo-physical Properties

Consideration of the electronic structure of the lanthanide ions explains their unique photo-physical properties (Figure 1 a). Coulomic interactions between 4f electrons give rise to terms exhibiting a large (of the order of 10^4 cm^{-1}) separation in energy. Spin-orbit coupling results in further splitting (of the order of 10^3 cm^{-1}) yielding a number of J-levels, described by the relevant Russell-Saunders component $^{(2S+1)}L_J$, where L is the orbital angular momentum, 2S + 1 is the spin multiplicity, and J the coupled f metal total angular momentum. A fine structure may be observed within associated spectral bands, arising from the crystal field, and thus potentially capable of providing information concerning the coordination environment. Population of higher energy states within the lanthanide manifold can lead to luminescence emission, this being most effective (long lived) from those states most separated from ground states (where non radiative loss is minimal).

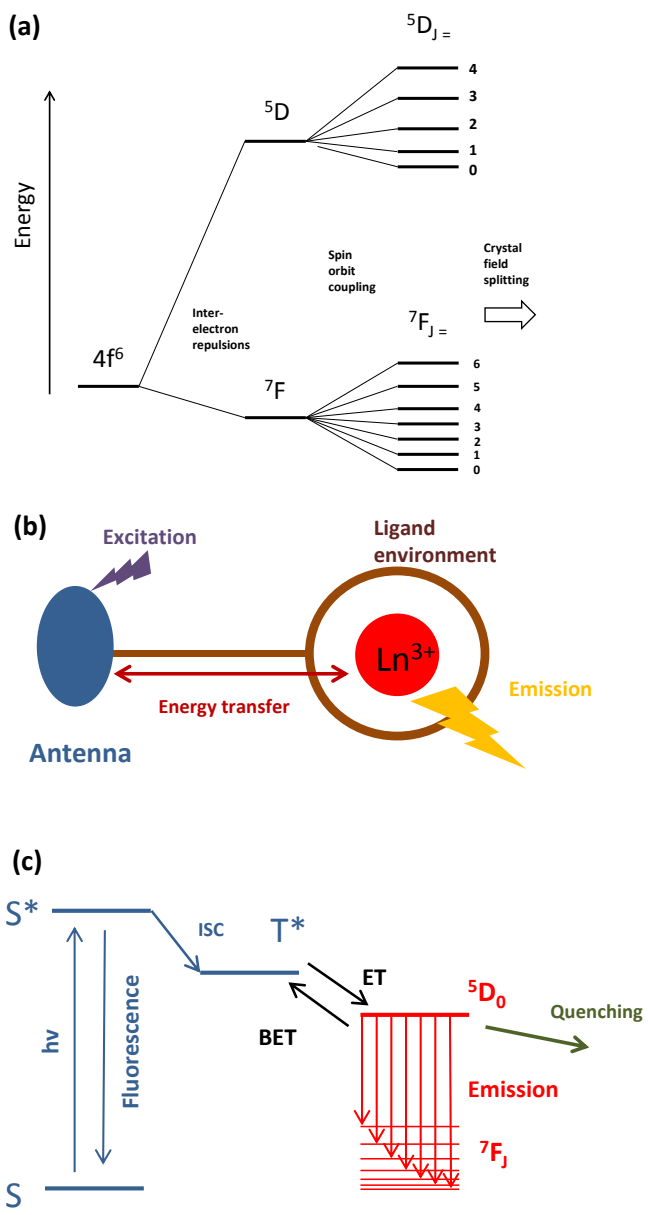

Figure 1. (a) Energy levels for the *[Xe] 4f⁶ 5d⁰* configuration of Eu^{3+}. Inter-electron repulsions lead to splitting and the ^5D and ^7F terms. These terms split further into J-levels as a result of spin orbit coupling. Subsequent crystal field splitting (not shown) leads to sub-levels associated with spectral fine structure. (b) Schematic of a lanthanide architecture incorporating an excitable antenna. (c) Energy level diagram depicting the photophysical processes involved in sensitised lanthanide emission (using Eu^{3+} as an example). Excitation of the antenna into a singlet excited state is followed by intersystem crossing to the triplet state; subsequent energy transfer yields the excited state of the lanthanide and radiative emission.

Symmetry imposed selection rules restrict formally allowed transitions to those associated with magnetic dipole excitation ($\Delta J = 0, \pm 1$; but not $J = 0 \rightarrow J = 0$). In reality, virtually no empirical examples of lanthanide complexes are truly centrosymmetric and electronic dipole transitions become possible though perturbation of parity by ligand field effects. Such electronic transitions, when they occur, are sensitive to the coordinating environment ("hypersensitive"), with asymmetric ligand fields generally leading to stronger (higher extinction) electronic transitions. [5, 20]

It remains the case, however, that direct magnetic or electronic dipole excitations are relatively weak (typically $\varepsilon \approx 0.1$ to 1 M^{-1} cm^{-1}) in comparison to fully allowed transitions observed in many other chromophores. To overcome this "limitation" sensitizer groups (or antenna) are often incorporated into the surrounding ligand environment to facilitate indirect excitation of the Ln^{3+} ion (Figure 1 b). Singlet excitation of the antenna is followed by intersystem crossing to its accessible triplet state and subsequent energy transfer to the lanthanide (Figure 1 c). The triplet excited state of the antenna must, of course, be higher than the lanthanide state to be populated but not so high that energetic alignment is poor – energy transfer will then be ineffective and antenna fluorescence will dominate. Similarly a triplet state too close in energy to the excited state will result in back energy transfer (BET), and hence no sensitisation. In principle, the mechanism of energy transfer (ET) can be either Forster, Dexter or a combination of the two. Dexter energy transfer occurs via a donor - acceptor orbital overlap, and is governed by an e^{-r} distance dependence. As orbital overlap is necessary for Dexter ET to occur, it generally only takes place over Angstrom scale distances unless the donor and acceptor orbital's are linked by a conjugated "bridge" (facilitating longer distance superexchange). Forster ET, in contrast, results from dipole-dipole interactions between the donor and the acceptor and follows a less sharply decaying r^{-6} distance dependence. Sensitization of lanthanide (III) complexes by coordinated d-block antenna has been shown to take place almost exclusively by Dexter ET[21] and same is assumed to be true for the vast majority of directly co-ordinated chromophores. It is however worth noting that for Yb^{3+} (and occasionally Eu^{3+}) sensitisation via the triplet state can be supplemented by a double electron transfer mechanism.[22, 23] Sensitization of lanthanides is not limited to organic chromophores, with transition metal complexes also being able to function as effective antenna via d block ligand to metal charge transfer excited states, with carboxylate-appended Re (I), Ru (II) and Os (II) $(bipyridyl)_3$ complexes having been associated with Ln.DO3A (Ln=Nd, Er, Yb) complexes, resulting in sensitized emission.[24]

Solution Based Lanthanide Assemblies

Self-Assembling and Sensing Emissive Systems

The possibility of sensitisation through a proximate antenna provides a means of engineering novel switching and sensing systems where emission in modulated by the presence, proximity or redox state of the antenna. The most straightforward, and perhaps effective, sensing and switching systems are examples where the antenna assembles directly with the lanthanide. Skabara and coworkers have reported the association of a tetrathiafulvalene carboxylate to a charge neutral DO3A complex, providing the first example of sensitization mediated by electron transfer from an electron-rich chromophore in a self-assembled system (Figure 2a).[23] This form of self-assembly can be exploited to efficiently screen a

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large number of potential sensitizers, with the work of Coe et al describing the evaluation of a number of carboxylate-modified d-metal complexes for their suitability as antenna.[24] Similarly, Gunnlaugsson and coworkers have reported the coordination to, and sensitisation of, coordinatively unsaturated Tb^{3+} cyclen-derived complexes by displacement of the metal-bound water molecules by salicylic acid in aqueous conditions.[25] Faulkner and co-workers have also exploited the coordination/sensitisation strategy by employing benzoic acid appended Eu^{3+} and Tb^{3+} DO3A complexes to investigate the pH dependent self-assembly of bimetallic lanthanide complexes (Figure 2b).[26] Lifetime measurements in H_2O and D_2O indicated a decrease of q (the number of bound H_2O molecules) from ~2 to ~1 at higher pH, indicating displacement of lanthanide-bound bound water upon deprotonation of the benzoic acid pendants. This change was not seen to occur when an ester analogue pendant was used, indicating that the complexes aggregate through bridging by the benzoate group. The formation of the dimer was further confirmed by mass spectroscopy.

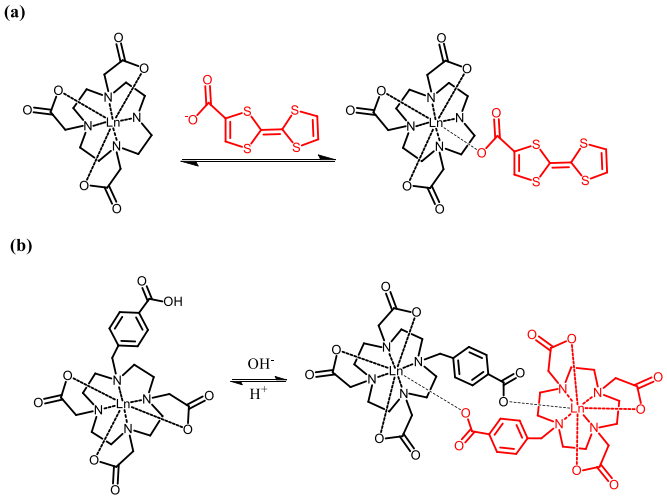

Figure 2. (a) Association to, and sensitisation of, a cyclen lanthanide complex by tetrathiafulvalene carboxylate ligation. (b) Formation of self-assembled dimetallic benzoic acid appended cyclen lanthanide complexes.

Further work by the same group has reported the ligation and sensitisation of seven coordinate DO3A complexes by a range of chromophore-bearing carboxylates and phosphonates.[27] The study focused on near IR emitting lanthanides (Yb, Nd, Er) which exhibit lower energy excited states, making sensitisation possible through a wider range of chromophores. While binding was found to be stronger for phosphonates than carboxylate ligands (due to a bidentate mode of co-ordination for the latter), this mode of complexation was only seen to be efficient with early lanthanides, with the binding pocket too sterically constrained for those ions later in the series and of lower radius.

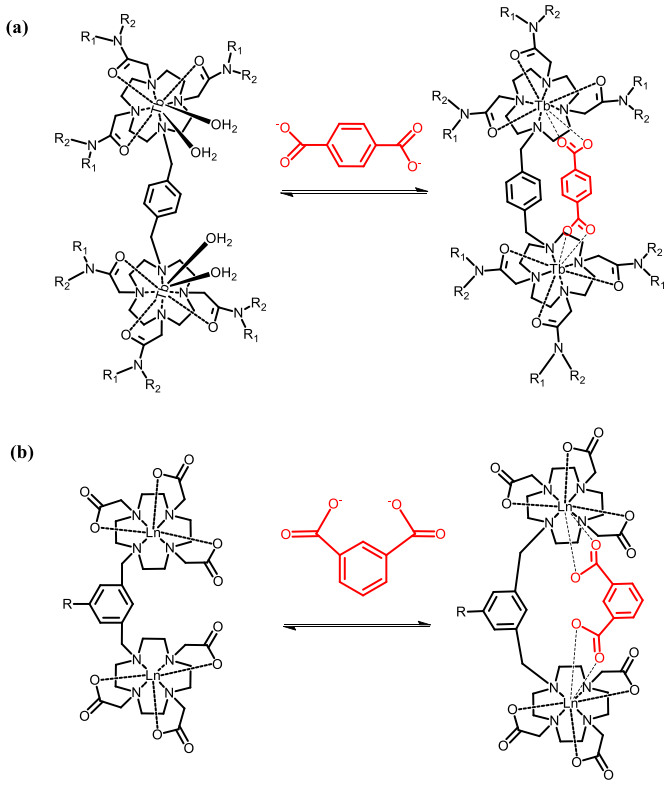

Figure 3. High affinity coordination of (a) terephthalic and (b) isophthalic acid to xylyl binuclear lanthanide complexes.

Ligation to covalently bound dinuclear lanthanide complexes has also been investigated, with Gunnlaugsson and coworkers reporting the binding of terephthalic acid to coordinatively unsaturated binuclear lanthanide complexes with binding constants exceeding10^4 in aqueous solution (Figure 3a).[28] Similarly, we have investigated the binding of a number of dicarboxylates with meta xylyl binuclear DO3A complexes (Figure 3b). Very high association constants (> 2 x 10^7 M^{-1}) were determined for the binding of isophthalic acid (with lower values for benzoic acid, phthalic acid and terephthalic acid) demonstrating a good fit into the coordination pocket of the xylyl binuclear DO3A complexes.[29] More recently we have applied the system to the surface recruitment of luminescent lanthanide complexes (see below).

In related work, Gunnlaugsson and coworkers have developed derived luminescent lanthanide displacement assays capable of sensing anions. The pH sensitive association β-diketonate to a cyclen based Eu^{3+} complex is reported. Sensitisation of the Eu^{3+} emission ceases upon displacement of the β-diketonate by various anions in aqueous conditions (Figure 4 a).[30]

While the direct binding of a sensitising entity of analytical interest clearly works, more sophisticated "indirect" methods based on triggered change in native antenna-lanthanide distance, have also been developed. Pierre and Thibon have reported, for example, a highly selective chemical K^+ sensor, based on triggered conformational changes upon target association. The sensor consists of a Tb.DOTA chelate separated from an azaxanthone antenna via a diaza crown ether coordination site, a lariat ether moiety and flexible linker (Figure 4b). K^+ binding in the crown ether coordination site (in anhydrous ethanol) results in an π –cation interaction between the lariat ether and the K^+ centre, locking the molecular architecture into a rigid conformation and bringing the azaxanthone into proximity of

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the Tb^{3+} centre, allowing for sensitized emission.[31] The assay showed good selectivity, with a 93 fold higher increase in emission intensity upon addition of K^+ in comparison to Na^+, and functions well in the clinically useful range of 0-10 mM with a 22 fold increase in luminescence intensity observed at 10 mM. (changes in extracellular and serum potassium levels have been linked to hypertension, stroke, and seizures).

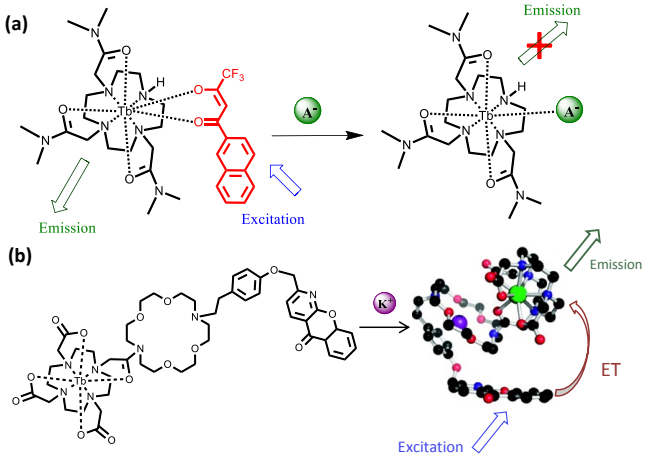

Figure 4. (a) Displacement assay developed by Gunnlaugsson and coworkers. Displacement of the β-diketonate antenna by anionic species leads to cessation of sensitised emission. (b) Potassium sensor developed by Pierre and Thibon. K^+ binding results in a conformational rearrangement that brings the azaxanthone antenna close enough to sensitise the Tb^{3+}. A 22 fold increase in emission intensity observed upon addition of 10 mM K^+ in anhydrous ethanol. The sensor showed high selectivity, with 93 fold higher enhancement of emission upon addition of K^+ compared to Na^+. Reprinted (adapted) with permission from A. Thibon and V. C. Pierre, J. Am. Chem. Soc., 2009, 131, 434. Copyright (2009) American Chemical Society.

The group of Parker has also focused on developing lanthanide based sensing systems allowing for selective detection of anions in aqueous solution.[2, 32] This has been achieved perturbation of a sensitizer ground or excited state by anion coordination to the antenna[33] or by direct association of the anion to the lanthanide centre.[34-38] One example describes the development of lactate and citrate sensors, with the anions serving as biomarkers for prostate cancer.[36] A number of sensitized (employing azathiaxanthone and azaxanthone antenna) Eu^{3+} complexes have also been examined for anion binding with a selectivity tuned by steric control at the metal centre. Suitably selective complexes were employed to prepare analytical curves for lactate and citrate detection by mapping changes in the relative intensities of the magnetic $^5D_0 \rightarrow {}^7F_1$ and electric dipole $^5D_0 \rightarrow {}^7F_2$ (the former insensitive to the to changes in the coordination environment) transitions. The assay was shown to be clinically useful, with a correlation between the measured citrate levels and the health status of the patients noted.[39]

Redox Switchable Systems

The integration of a redox addressable moiety into appropriate supramolecular architectures can lead, through appropriate design, to an ability to switch sensitised emission electrochemically. In one simple example of this, Schneider and coworkers have utilised a bridging and reduceable disulphide bond between carbostyril antenna and diethylenetriaminepentaacetic Tb^{3+} centres (Figure 5 a).[4] Reduction of disulphide bond with (tris(2-carboxyethyl)phosphine) in aqueous buffer, leads to increased conformational freedom, allowing the antenna reside further from the Tb^{3+} centre and leading to a reduction in sensitised emission.

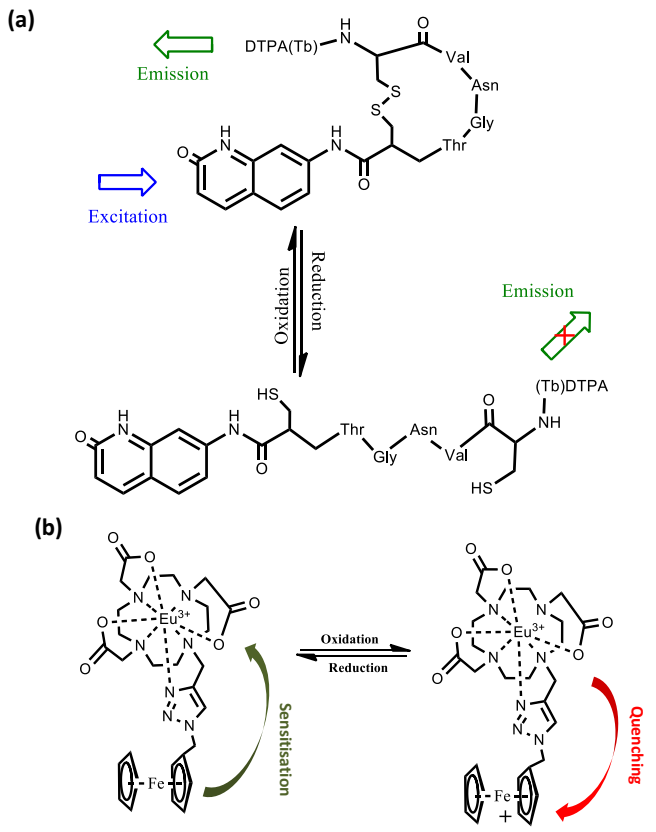

Figure 5. (a) Redox lanthanide emission switch based on conformational changes within the architecture upon breaking of a disulphide bond under reducing conditions. (b) Redox switching of a d-f dyad. Oxidation of the ferrocene sensitizer to the quenching ferrocenium moiety brings about a cessation in emission.

Redox switching of sensitized lanthanide emission can also be brought about by affecting the redox state of the antenna directly. Recently we have demonstrated the switchable emission of a ferrocene-europium dyad (Figure 5 b) obtained via Huisgen cycloaddition of a propargyl DO3A to a ferrocene azide.[6] In its reduced state the ferrocene acts to sensitise Eu^{3+} emission. However, when oxidised, the quenching ferrocenium ion leads to a reduction of Eu^{3+} emission with excellent reversibility. Similar reversible emission switching was also observed for the Yb^{3+} analogue.

Interlocked Lanthanide Assemblies

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An ever increasing interest is being shown in the construction of mechanically bonded molecules as integral components of molecular switches[9, 10] data storage[14] and topologically unique sensing systems.[40] Luminescent species have been integrated into such structures as a means of transduction where triggered motion, conformational changes or chemical binding are monitored through luminescence emission. Recently, there have been a number of reports integrating luminescent species into (primarily static) interlocked systems[15, 17-19, 41, 42].

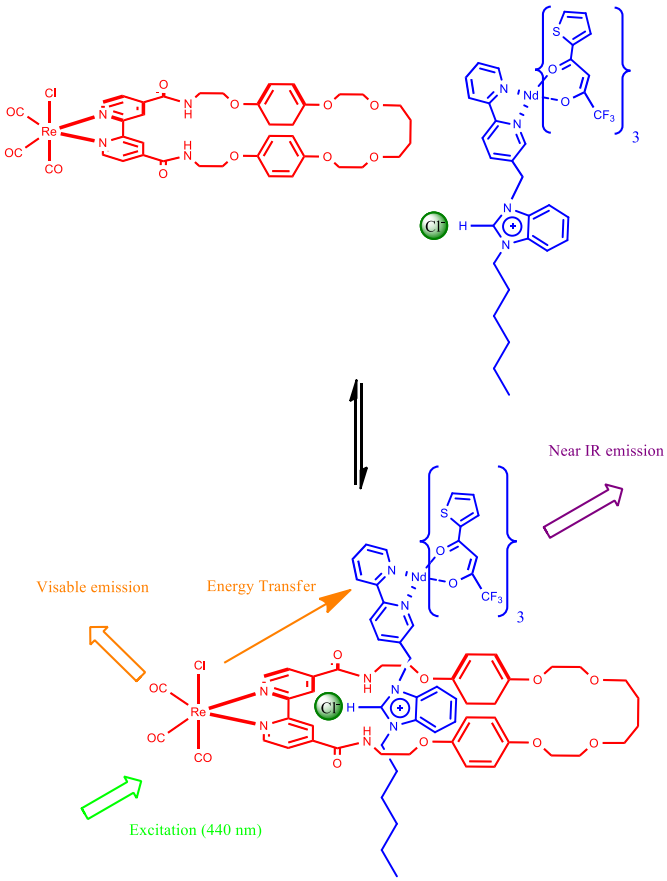

Figure 6. Anion templated assembly of a d-f heteronuclear [2]pseudorotaxane, exhibiting sensitised lanthanide luminescence. Anion templated threading in non-competitive media allows for sensitisation of the Nd^{3+} stoppered axle via the Re appended macrocycle.

In one example, we have reported the anion templated assembly of a d-f heteronuclear [2]pseudorotaxane (Figure 6).[43] The macrocyclic component consists of a transition metal rhenium(I) bipyridyl metal sensitizer and isophthalamide based anion recognition site, with the axle incorporating a imidazolium cation and luminescent neodynium stopper. Upon pseudorotaxane formation by chloride templated threading, excitation of the rhenium(I) bipyridyl metal antenna leads to sensitisation of the neodymium and near IR emission.

Significant work on interpenetrative pseudorotaxane emissive lanthanide assemblies has also been reported by the group of Lui. In an early example[44] (Figure 7) the assembly of three pyridine-2,6-dicarboxylic acid (DPA) ligands, appended to an electron rich dibenzo-24-crown-8 macrocycle resulted in a complex exhibiting the characteristic Tb^{3+} fingerprint emission. Threading of a guest incorporating an electron deficient dialkylammonium binding site and a ferrocene moiety, into the crown ether macrocycle, resulted in significant loss of lanthanide emission, attributed to an intramolecular photo-electron transfer process from the ferrocene units to the DPA moieties. Emission could be reversibly recovered by addition of KPF_6, with K^+ demonstrating stronger (K_a = 7.6 × 10^3 M^{-1}) association with the crown binding site than the dialkylammonium cation (K_a = 1.2 × 10^3 M^{-1}) in a $CH_3CN/CHCl_3$ mixed solvent system. Subsequent addition of 18-crown-6 (18C6) to the solution lead to the restoration of quenching, demonstrating reversible host/guest complexation.

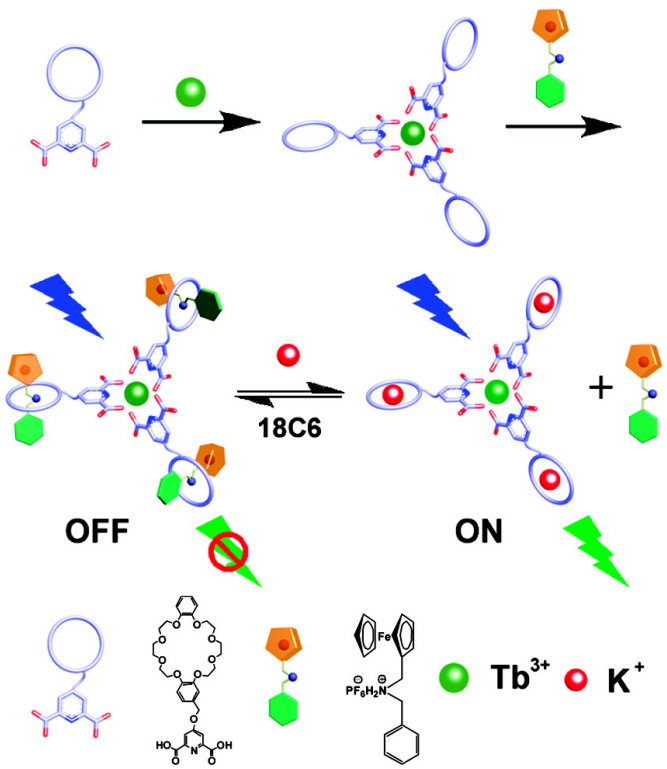

Figure 7. Association of crown appended DPA ligands to Tb^{3+} followed by threading of dialkylammonium ferrocene guest leading to quenching of lanthanide emission. Displacement of the ferrocene guest with the more strongly associating K^+ ion replenishes emission, a change itself reversible by addition of 18-crown-6 (18C6). Reprinted (adapted) with permission from M. Han, H.-Y. Zhang, L.-X. Yang, Q. Jiang and Y. Liu, Org. Lett., 2008, 10, 5557. Copyright (2008) American Chemical Society.

In related work by the same group, the interpenetration of a fullerene-stoppered dialkylammonium threading component through a Tb^{3+}-recruiting and sensitizing terpyridine-appended crown macrocycle was reported to result in the formation of a [2]pseudorotaxane assembly in $CH_3CN/CHCl_3$ (Figure 8).[45] While terpyridine sensitized Tb^{3+} emission was strong in the case of the unthreaded macrocycle, the presence of the thread (and specifically its derived [2]pseudorotaxane) was seen to quench emission via PET from the excited Tb^{3+} singlet state to

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the fullerene. Again cessation of threading and the return of emission could be affected by the addition of K^+ guest species, which displace the thread from the crown macrocycle, a process which is, again, reversible.

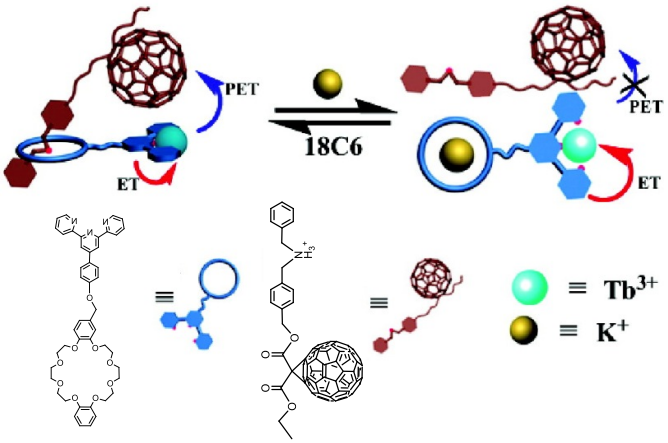

Figure 8. Reversible formation of fullerene/terbium containing [2] pseudo-rotaxane. Association leads to quenching of the sensitized terbium emission. Competitive dethreading on addition of K^+ leads to a return of terbium emission, a process reversible by addition of 18C6. Reprinted (adapted) with permission from Z.-J. Ding, Y.-M. Zhang, X. Teng and Y. Liu, J. Org. Chem., 2011, 76, 1910. Copyright (2011) American Chemical Society.

In a more recent report the group has demonstrated [2]pseudorotaxane formation between a diarylperfluorocyclopentene axle and a lanthanide europium tagged crown macrocycle, again employing the dialkylammonium/crown interaction (Figure 9).[46] The threading component was seen to exhibit reversible and stable photo-chromism, with switching between the open and closed forms achieved by visible and UV irradiation, respectively. While threading of the open form led to only negligible changes in emission, UV irradiation of the pseudorotaxane to the closed form brought about a ~80% decrease in Eu^{3+} emission intensity suggesting an initiated resonance energy transfer (RET) from the Eu^{3+} ion to the diheteroarylethene acceptor, i.e, a reversible optically modulated intermolecular sensitisation.

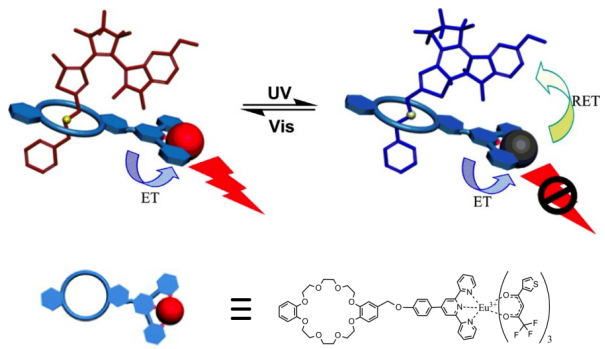

Figure 9. Photochromism between the open form and closed form of the axle in a lanthanide containing pseudorotaxane allowing for optical control of Eu^{3+} luminescence quenching, and hence photo-switchable emission. Reprinted (adapted) with permission from H.-B. Cheng, H.-Y. Zhang and Y. Liu, J. Am. Chem. Soc., 2013, 135, 10190. Copyright (2013) American Chemical Society.

We have reported the preparation of the first interlocked lanthanide appended [2]rotaxane (Figure 10a),[47] prepared by a chloride templated clipping reaction between a diamine macrocycle precursor and 5-azidoisophthaloyl chloride. It has been demonstrated that this anion templation strategy results in the formation of a unique three dimensional anion binding cavity incorporating electron-deficient pyridinium (axle) and amide protons (macrocycle) components,.[48, 49] The azido group on the macrocycle was subsequently used to attach propargyl Eu.DO3A via Huisgen cycloaddition, with the objective of using the lanthanide emission characteristics as a method of detecting selective chloride binding in the three dimensional cavity. Chloride binding in polar organic solvents was probed by sensitised (via the aryl chromomophore) Eu^{3+} emission, with an initial decrease of luminescence intensity, and a change in the hypersensitive $\Delta J = 2$ transition, observed upon its addition, (suggesting perturbation of the Eu^{3+} ligand field and direct co-ordination of the anion to the lanthanide centre rather than in the three dimensional anion binding cavity). The intensity decrease was followed by a chloride specific increase, indicative of a second binding event attributed to association of Cl^- with the anion binding cavity.

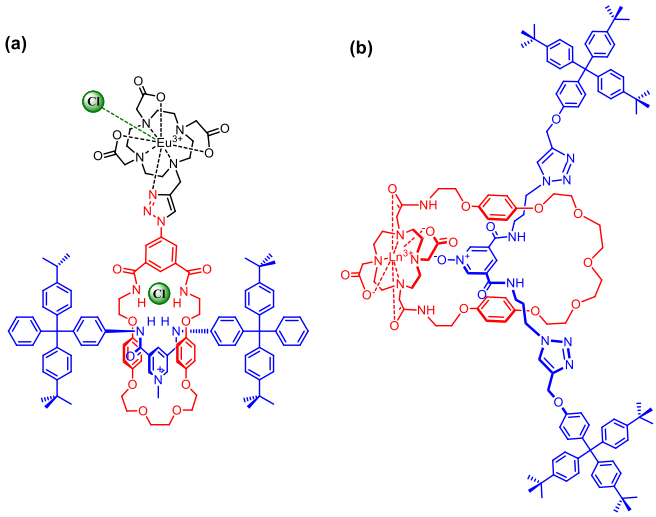

Figure 10. (a) Fully interlocked anion templated [2]-Rotaxane incorporating a Eu.DO3A complex. Coordination of chloride occurs both in the three dimensional anion cavity sites and at the Europium centre. (b) Lanthanide-cation templated rotaxane. Templation is achieved by interaction of the N-oxide moiety with the lanthanide centre.

More recently we have described the lanthanide-cation templated synthesis of a lanthanide-containing rotaxane.[50] Initial pseudorotaxane formation was achieved by the threading of a bis azide terminated axle precursor, incorporating a pyridine N-oxide component, through a lanthanide appended macrocycle by virtue of the interaction between the pyridine N-oxide oxygen and the lanthanide cation. Stoppering was subsequently achieved by click reaction of alkyne terminated stopper at the thread azide termini (Figure 10b).

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Surface Assembled Lanthanide Architectures

In facilitating both progression to more realistic device formats and an amplification of any triggered emission changes that occur at molecular scales, the controlled surface assembly of responsive lanthanide structures is required. To date, however, progress in this vein has been limited.[10, 51, 52] Gunnlaugsson and coworkers have shown that the assembly of thiolated cyclen SAMs can be followed by solution phase recruitment of sensitised beta-diketonate ligands and detectable emission when C12 spacer units are employed.[53, 54] We have recently reported the first example of simultaneous, reversible recruitment and sensitisation of lanthanide complexes at ligating molecular films. In building on previous work (discussed above) in which the strong ($K_a > 2 \times 10^7$ M^{-1}) association of xylyl binuclear lanthanide complexes with isophthalic acid (IPA)[29] was demonstrated, the recruitment, and sensitized emission, of these complexes at gold substrates (Figure 11) was specifically investigated.[55] Lanthanide complex recruitment at the IPA decorated interfaces was confirmed by the observation of the Tb^{3+} and Eu^{3+} fingerprint emission characteristics and film thickness changes as monitored by ellipsometry. The pH dependent nature of the association was consistent with association of the (hard ionic) deprotonated carboxylic acid groups with the lanthanide centres. Upon varying the IPA tether length, and hence the lanthanide distance from the interface, an exponential increase in emission intensity was observed, consistent with the known luminescence quenching properties of metallic surfaces.[56-59]

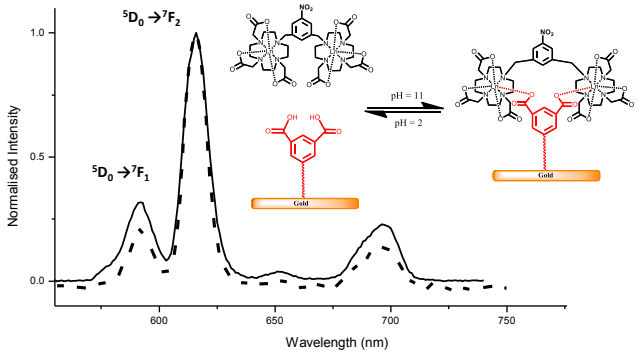

Figure 11. pH dependent reversible recruitment of xylyl binuclear lanthanide complexes to isophthalic acid decorated gold interfaces giving rise to sensitised Eu^{3+} emission (---); when the spectrum is compared with that of the solution species (—) the near-equivalent $^5D_0 \rightarrow {}^7F_1$ and hypersensitive $^5D_0 \rightarrow {}^7F_2$ relative emission intensities are noted. Reprinted (adapted) with permission from J. Lehr, J. Bennett, M. Tropiano, T. J. Sorensen, S. Faulkner, P. D. Beer and J. J. Davis, Langmuir, 2013, 29, 1475. Copyright (2013) American Chemical Society.

The work of Gulino and coworkers avoids the difficulties associated with surface quenching by attachment of presensitized luminescent (5-amino-1,10- phenanthroline) tris (dibenzoylmethane) Eu^{3+} on fused non-conducting silica substrates with the resulting surfaces exhibiting strong Eu^{3+} luminescence.[60] Attachment of the same moiety to Si(100) substrates resulted apparently weaker emission, possibly due to energy loss to the supporting semiconductor. [61]

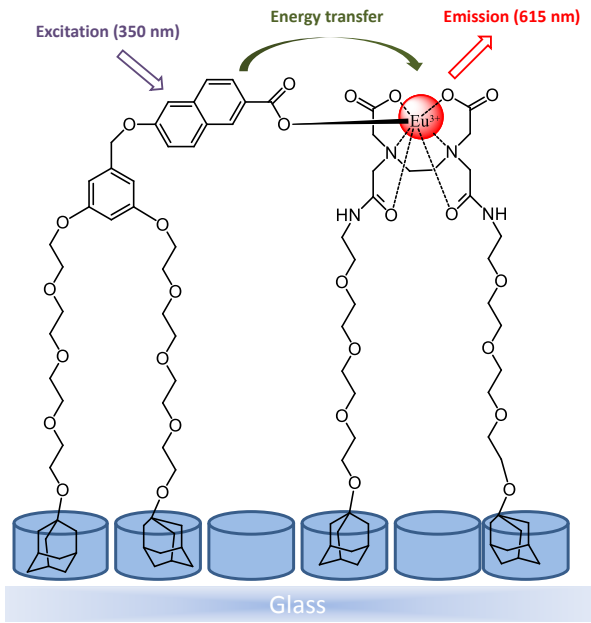

Figure 12. Surface co-immobilised Eu.EDTA complex and carboxyl ligand containing naphthalene sensitizer on cyclodextrin molecular printboards on glass. Intermolecular coordination leads to effective and imageable sensitised Eu^{3+} emission.

Similarly the work of Huskins and co-workers has focused on the recruitment of Eu^{3+} complexes on glass. Co-immobilisation of Eu.EDTA complex and a carboxyl ligand containing naphthalene sensitizer on a cyclodextrin glass print board was, for example, achieved by micro-contact printing (Figure 12) in the establishment of mixed films where neighbouring intermolecular interactions were sufficient to generate strong emission.[62] In an interesting extension, an analogous architecture has been applied to the development of sensing systems. The recruitment of β-diketotone naphthalene to Eu.EDTA printboards resulted in sensitisation of the lanthanide via the recruited ligand; displacement of the antenna by the analyte (an anthrax biomarker) could be observed through a cessation of emission. The system has been incorporated into a microfluidic device.[63]

The assembly of lanthanides at interfaces has not been restricted to planar substrates. In an extension of their solution work (discussed above) Gunnlaugsson and coworkers have developed anion-sensing gold nanoparticles (AuNPs) utilising lanthanide luminescence to achieve transduction. Decoration of AuNPs with Eu.DO3A complex (tethered via an alkylthiol spacer) was followed by (pH sensitive[53]) naphthalene β-diketone antenna recruitment, resulting in luminescence. Displacement of the sensitising group led to a decline of emission. [54] The group have employed the same AuNPs- Eu cyclen architecture in the development of sensors. Sensitisation by naphthalene β-diketone antenna recruitment resulted in luminescence, which was seen to cease in the presence of BSA, an observation attributed to a quenching effect, rather than displacement (Figure 13).[64] It was suggested that the

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competitive displacement of the quenching BSA could be applied in drug sensing.

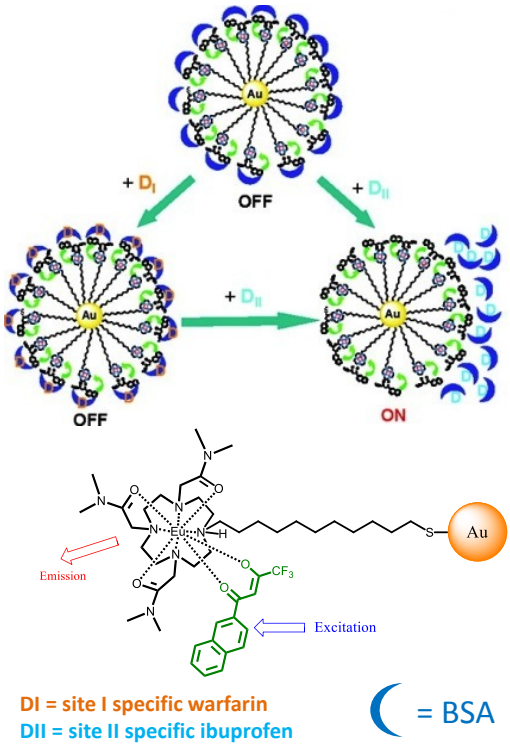

Figure 13. BSA recruitment to Eu.DO3A β-diketone modified gold nanoparticle results in a loss of sensitised emission due to luminescence quenching. Addition of a BSA site II specific drug (ibuprofen, DII) initiated competitive binding to the BSA moiety leading to a restoration of emission. In contrast addition of BSA site I drug (warfarin DI) resulted in no increase of emission intensity. Reprinted (adapted) with permission from. Comby and T. Gunnlaugsson, ACS Nano, 2011, 5, 7184. Copyright (2011) American Chemical Society.

Pikramenou and coworkers have also presented AuNPs decorated with thiolated diethylene triamine pentaacetic acid Eu^{3+} complexes.[65] More recently, Yan and coworkers[66] have described the modification of oxidised gallium nitride particles with an imidazolium salt ionic liquid by employing silane chemistry. Subsequent anion exchange with a tetrakis β-diketonate Eu^{3+} complex results in the electrostatically driven assembly of the lanthanide complex at the particle interface. Broad excitation at 360 nm suggests sensitisation through the β—diketonate and the gallium nitride matrix, and yielded fingerprint europium emission bands.

In a recent demonstration of surface assembly, sensitisation and redox switching emission, we have reported the recruitment of (mononuclear) DO3A complexes to catechol decorated gold interfaces.[55] Sensitized lanthanide emission was observed upon excitation at the characteristic catechol absorption wavelength (λ = 290 nm). In conjunction with pH dependent recruitment, this is indicative of the ligation of the complex to the surface bound ligand. Notably, electrochemical oxidation of the catechol moiety to its quinone form results in a loss of lanthanide emission, suggesting a cessation of ligation (electrochemically switchable recruitment and emission, Figure 14).

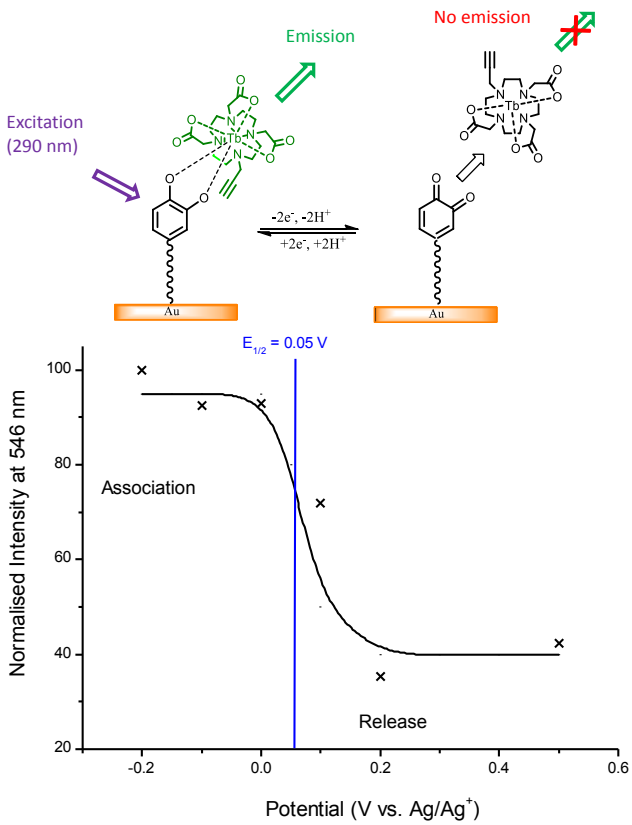

Figure 14. Ligating catechol films on gold allowing for the electrochemically reversible recruitment and sensitisation of Tb.DO3A complexes. Above the redox potential of the catechol (0.05 V vs. Ag/Ag^+) the films are oxidised resulting in a cessation of binding and release of the luminescent lanthanide complex. Reprinted (adapted) with permission from J. Lehr, J. Bennett, M. Tropiano, T. J. Sorensen, S. Faulkner, P. D. Beer and J. J. Davis, Langmuir, 2013, 29, 1475. Copyright (2013) American Chemical Society.

Conclusions

The incorporation of emitting lanthanide species into supra-molecular architectures offers a potent method of sensing coordinative, conformational and electronic change. While only a relatively limited number of such systems have been described to date, these have already underlined both mechanisms of assembly and the considerable potential offered through exploiting the unique spectral characteristics of lanthanides in sensing and switching supramolecular architectures. As our ability to synthesise increasingly complex molecular constructs and to integrate them into diffusively mobile or robustly switchable configurations continues apace, we can expect the considerable functional potential of lanthanides to be progressively realised.

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