Tailored Receptors for Supramolecular Lanthanide Devices

Claude Piguet*

Although the lanthanide metal ions, LnIII, are considered as the 'chameleons' of coordination chemistry because of their weak dative bonds with common ligands, their variable coordination numbers, and limited stereochemical preferences, their peculiar 4f electronic configurations have attracted much attention for the design of molecular devices such as contrast agents in MRI, shift reagents in NMR, luminescent stains for fluoroimmunoassays and DNA labelling, and catalysts for selective RNA sequencing [1]. A close structural control of the coordination site and the incorporation of soft bipyridine and hard salicylamide binding sites. In the presence of a single Fe ion, and depending on its oxidation state, this latter coordinates selectively to one or the other site, displaying very characteristic properties in each case.

Upon oxidation or reduction, the metal ion translocates reversibly, thus allowing information storage. This molecular device can be addressed by various means, including chiroptical-, Mössbauer-, optical spectroscopy as well as magnetochemical methods (Fig. 4).

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accessibility of Ln$^{III}$ are crucial in these functional molecular devices, and the use of the Lock and Key principle associated with macrocyclic receptors has led to remarkable successes [2]. However, the fine-tuning of the Ln$^{III}$ coordination sphere required for i) the selective recognition of the various Ln$^{III}$ according to their size and ii) the control of electronic, magnetic, and spectroscopic properties is often not reached with rigid preorganized receptors. A new approach based on the Induced Fit concept [3] involves the simultaneous coordination and wrapping of judiciously designed tridentate strands about Ln$^{III}$ to give discrete lanthanide building blocks with tunable structural and electronic properties resulting from subtle secondary interactions [1].

Ligands $L^i$ ($i = 1-3$) are prototypes of such strands and they form mononuclear three-bladed propellers $[\text{Ln}(L^i-2H)]^{3+}$ and $[\text{Ln}(L^i)]^{3+}$ ($i = 2, 3$) upon reaction with Ln$^{III}$ [4][5]. The 1:3 complexes $[\text{Ln}(L^i-2H)]^{3-}$ are well-known for the complete lanthanide series and fulfill some important requirements for the design of Ln$^{III}$ sensors with predetermined properties: i) they are stable in water, ii) possess well-protected coordination sites, and iii) display strong luminescence with Eu$^{III}$ and Tb$^{III}$ [4]. However, the lack of selectivity for the coordination of different Ln$^{III}$ and the limited structural and electronic control associated with terminal carboxylic side arms lead us to focus on the ester ($L^2$) and amide ($L^3$) derivatives [5]. As expected from the strong electron-attracting effect of ethoxy substituents, the carbonyl groups in $L^2$ are poorly coordinating leading to unstable 1:3 complexes in acetonitrile (Fig. 1). Only pure 1:2 complexes can be isolated in the solid state, and the crystal structure of $[\text{Eu}(L^2)_{2}(OH)_{2}(OTf)_{2}]$ reveals anomalously long Eu-O(carbonyl) bond distances [5]. The use of $N,N'$-diethylcarbamoyl side arms in $L^3$ leads to more stable three-bladed propellers $[\text{Ln}(L^3)]^{3+}$ where Ln$^{III}$ is nine-coordinated in a pseudo-tricapped trigonal prismatic site produced by the three wrapped strands. The cumulative stability constants $\log(B_3)$ show a smooth increase with decreasing Ln$^{III}$ ionic radii attributed to electrostatic effects (Fig. 1), but the crystal structures of $[\text{Ln}(L^3)]^{3+}$ (Ln = La, Eu) together with paramagnetic NMR studies in solution establish that the contraction of the coordination sphere required for the complexation of heavy Ln$^{III}$ significantly affects the wrapping of the tridentate units leading to two different isostructural series according to the size of Ln$^{III}$ [5]. The binding of extended aromatic benzimidazole side arms to the central pyridine ring in $L^4$ provides sufficient interstrand stacking interactions in the mononuclear triple-helical complexes $[\text{Ln}(L^4)]^{3+}$ to
Towards the Synthesis of Functionalized Ribonucleic Acids

Stefan Pitsch*

Current Research Topics

Being fascinated by the structure and the biological function of nucleic acids, I would like to contribute to their research. As a synthetic chemist, I am planning to investigate the synthesis, properties, and potential applications of functionalized oligonucleotides. Thereby, I am concentrating on the (so far) less intensely investigated ribonucleic acid (RNA). About one year ago, I started developing a strategy for the synthesis of C(5')-functionalized nucleoside building blocks and RNA oligonucleotides derived therefrom, and have chosen (unnatural) L-configured RNA as a first

metals have been introduced to induce new electronic and structural properties in the final LnIII devices (Fig. 2). [Eu(L3)]3+ acts as an efficient and water-resistant UV→vis light-converting device [7], [LnFe(L3)]3+ exhibit subtle synergistic effects between the two metallic sites leading to the fine tuning of the P6_3 spin-crossover parameters [8], and [LnCo(L3)]3+ instead represent the first inert facial non-covalent podates obtained with LnIII as templating agents [9].

These self-organized non-covalent lanthanide podates offer fascinating possibilities for the molecular and supramolecular programmation of structural and electronic properties in LnIII devices. They are currently investigated as prototypes for i) selective recognition of LnIII, ii) directional vis→vis light conversion, iii) coupled optical-magnetic switches, and iv) luminescent metallopolymers.

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