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can then be transferred to a softer nitrogen ligand sphere, such as porphyrins, better suited to its oxidation state. 2) Protonation of the Fe<sup>III</sup>/siderophore, favoring its release. 3) Enzymatic degradation of the siderophore.

In order to mimic the iron release-incorporation mechanism, we [9] and others [10] have designed tripodal ligands

incorporating 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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- [1] J. Ott, G.M. Ramos Tombo, B. Schmid, L.M. Venanzi, G. Wang, T.R. Ward, *Tetrahedron Lett.* **1989**, 30, 6151.
- [2] T.R. Ward, L.M. Venanzi, A. Albinati, F. Lianza, T. Gerfin, V. Gramlich, G.M. Ramos Tombo, *Helv. Chim. Acta* **1991**, 74, 983.
- [3] T.R. Ward, P. Alemany, R. Hoffmann, *J. Phys. Chem.* **1993**, 97, 7691.
- [4] L. Giannini, E. Solari, S. De Angelis, T.R. Ward, C. Floriani, A. Chiesi-Villa, C. Rizoli, *J. Am. Chem. Soc.* **1995**, 117, 5801.
- [5] For a recent review see: T. Auf der Heyde, *Angew. Chem. Int. Ed.* **1994**, 33, 823.
- [6] H.H. Brintzinger, D. Fischer, R. Mühlhaupt, B. Rieger, R.M. Waymouth, *Angew. Chem. Int. Ed.* **1995**, 34, 1143.
- [7] O. Reiser, *Angew. Chem. Int. Ed.* **1993**, 32, 547, and refs. cited therein.
- [8] T.R. Ward, *Organometallics* **1996**, 15, 2836.
- [9] A. Lutz, T.R. Ward, M. Albrecht, *Tetrahedron* **1996**, 52, 12197.
- [10] L. Zelikovich, J. Libman, A. Shanzer, *Nature* **1995**, 374, 790.

## Tailored Receptors for Supramolecular Lanthanide Devices

Claude Piguet\*

Although the lanthanide metal ions, Ln<sup>III</sup>, 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<sup>n</sup> 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



Claude Piguet was born in Geneva (Switzerland) in 1961. He studied chemistry at the University of Geneva and received his M.S. degree in Chemistry in 1986. From 1986 to 1989, he was a graduate student at the Department of Inorganic Chemistry of the University of Geneva, where he obtained his Ph.D. thesis with felicitations in 1989 in the domain of coordination chemistry and dioxygen complex-

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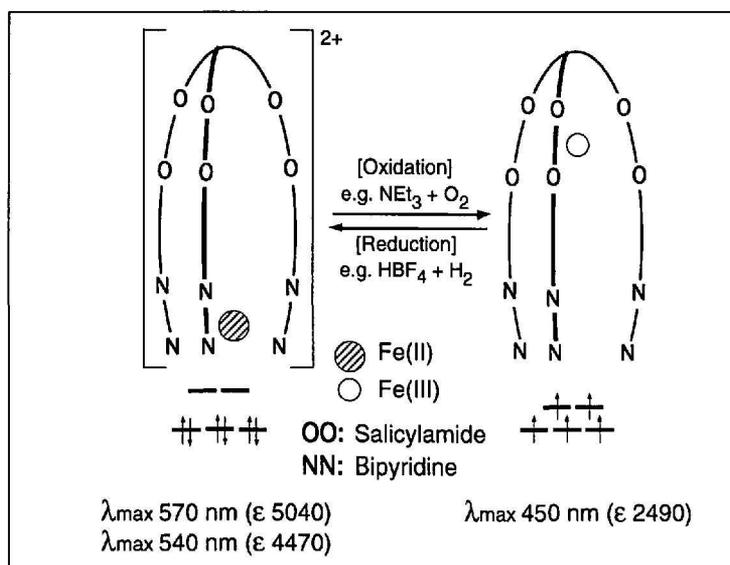


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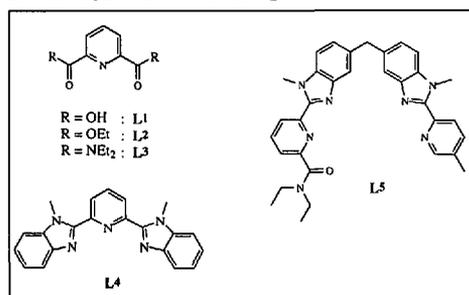
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accessibility of  $\text{Ln}^{\text{III}}$  are crucial in these functional molecular devices, and the use of the Lock and Key principle associated with macropolycyclic receptors have led to remarkable successes [2]. However, the fine tuning of the  $\text{Ln}^{\text{III}}$  coordination sphere required for *i*) the selective recognition of the various  $\text{Ln}^{\text{III}}$  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  $\text{Ln}^{\text{III}}$  to give discrete lanthanide building blocks with tunable structural and electronic properties resulting from subtle secondary interactions [1].

Ligands  $\text{L}^i$  ( $i = 1-3$ ) are prototypes of such strands and they form mononuclear three-bladed propellers  $[\text{Ln}(\text{L}^1\text{-2H})_3]^{3-}$  and  $[\text{Ln}(\text{L}^i)_3]^{3+}$  ( $i = 2, 3$ ) upon reaction with



$\text{Ln}^{\text{III}}$  [4][5]. The 1:3 complexes  $[\text{Ln}(\text{L}^1\text{-2H})_3]^{3-}$  are well-known for the complete lanthanide series and fulfil some important requirements for the design of  $\text{Ln}^{\text{III}}$  sensors with predetermined properties: *i*) they are stable in water, *ii*) possess well-protected coordination sites, and *iii*) display strong luminescence with  $\text{Eu}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$  [4]. However, the lack of selectivity for the coordination of different  $\text{Ln}^{\text{III}}$  and the limited structural and electronic control associated with terminal carboxylic side arms lead us to focus on the ester ( $\text{L}^2$ ) and amide ( $\text{L}^3$ ) derivatives [5]. As expected from the strong electron-attracting effect of ethoxy substituents, the carbonyl groups in  $\text{L}^2$  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  $[\text{Eu}(\text{L}^2)_2(\text{OH}_2)(\text{OTf})_2] \cdot (\text{OTf})$  reveals anomalously long Eu-O(carbonyl) bond distances [5]. The use of *N,N'*-diethylcarbamoyl side arms in  $\text{L}^3$  leads to more stable three-bladed propellers  $[\text{Ln}(\text{L}^3)_3]^{3+}$  where  $\text{Ln}^{\text{III}}$  is nine-coordinated in a pseudo-tricapped trigonal prismatic site produced by the three wrapped strands. The cumulative stability constants  $\log(\beta_3)$  show a smooth increase with decreasing  $\text{Ln}^{\text{III}}$  ionic radii attributed to elec-

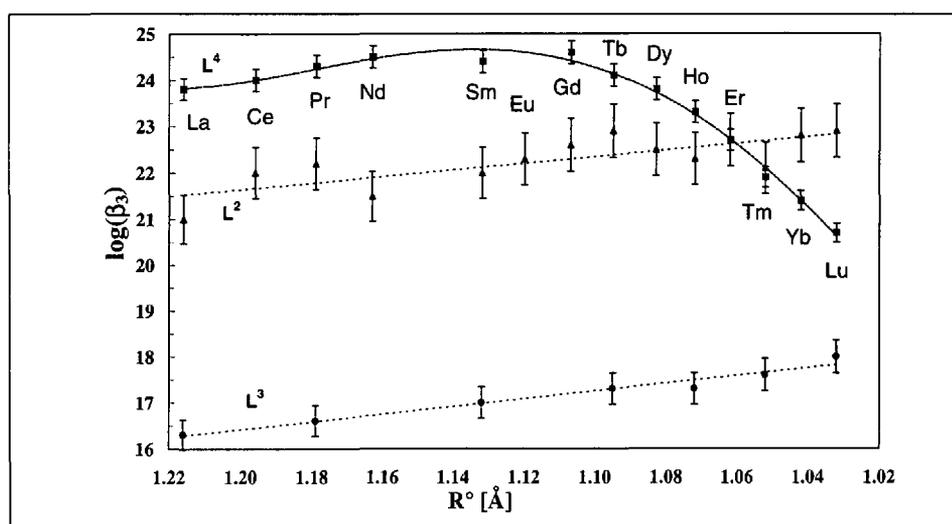


Fig. 1. Cumulative stability constants  $\log(\beta_3)$  for complexes  $[\text{Ln}(\text{L}^i)_3]^{3+}$  ( $i = 2-4$ ) in acetonitrile at  $25^\circ$

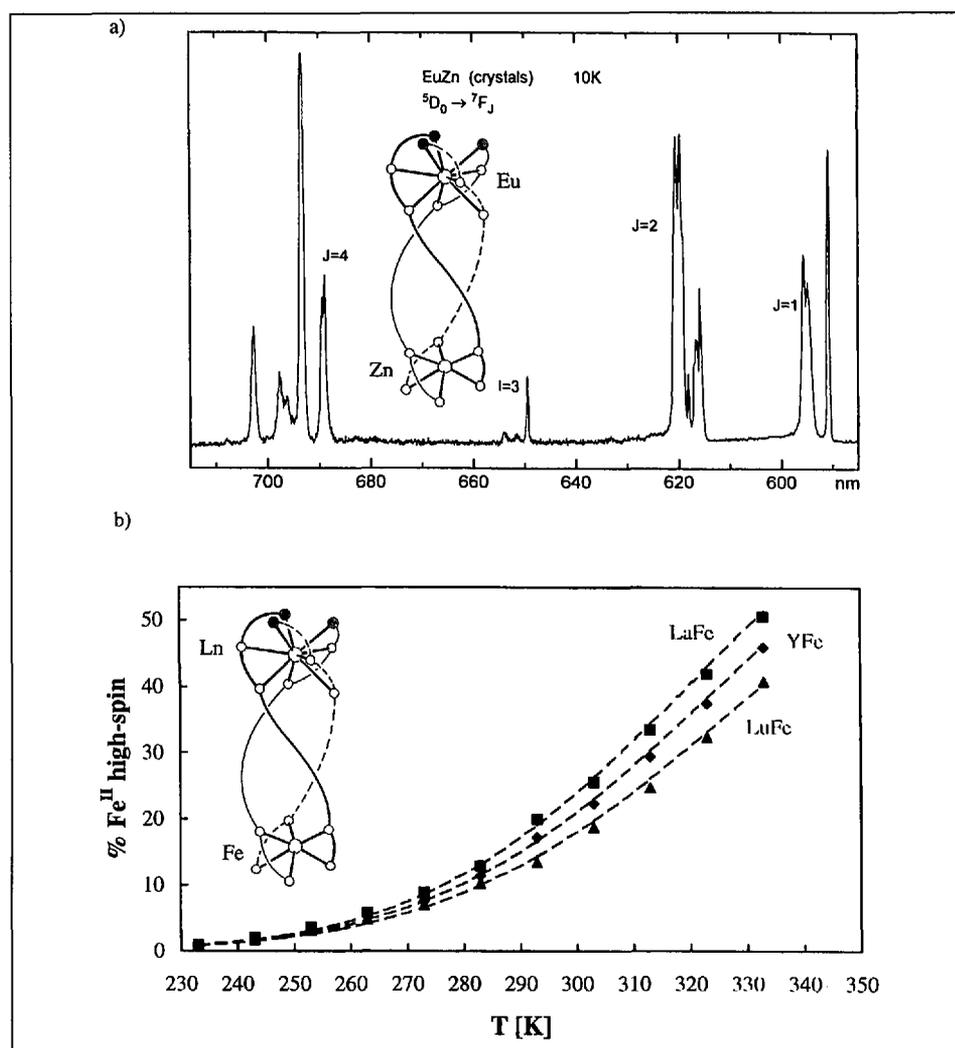


Fig. 2. a)  $[\text{EuZn}(\text{L}^5)_3]^{5+}$  as a UV  $\rightarrow$  vis light-converting device: emission spectrum under excitation through the ligand levels ( $\lambda_{\text{exc}} = 395 \text{ nm}$ ) and b)  $[\text{LnFe}(\text{L}^5)_3]^{5+}$  as tunable  $\text{Fe}^{\text{II}}$  spin-crossover devices: increasing fraction of  $\text{Fe}^{\text{II}}$  high spin for  $[\text{LnFe}(\text{L}^5)_3]^{5+}$  ( $\text{Ln} = \text{La}, \text{Y}, \text{Lu}$ ) in acetonitrile

trostatic effects (Fig. 1), but the crystal structures of  $[\text{Ln}(\text{L}^3)_3]^{3+}$  ( $\text{Ln} = \text{La}, \text{Eu}$ ) together with paramagnetic NMR studies in solution establish that the contraction of the coordination sphere required for the complexation of heavy  $\text{Ln}^{\text{III}}$  significantly affects the wrapping of the tridentate units

leading to two different isostructural series according to the size of  $\text{Ln}^{\text{III}}$  [5]. The binding of extended aromatic benzimidazole side arms to the central pyridine ring in  $\text{L}^4$  provides sufficient interstrand stacking interactions in the mononuclear triple-helical complexes  $[\text{Ln}(\text{L}^4)_3]^{3+}$  to

give a broad peak of selectivity around  $[\text{Gd}(\text{L}^4)_3]^{3+}$ , for which interstrand  $\pi$ -stacking interactions are optimized (Fig. 1) [6]. Unfortunately, only faint luminescence is observed for  $[\text{Eu}(\text{L}^4)_3]^{3+}$ , probably as the result of efficient non-radiative quenching processes via low-energy excimer states [6].

Suitable tridentate binding units for triple-helical lanthanide building blocks derived from these structural motives thus require the simultaneous connection of benzimidazole and amide side arms to the central pyridine ring leading to unsymmetrical tridentate binding units. In order *i*) to increase structural control and *ii*) to prevent MER  $\rightarrow$  FAC isomerization of the triple-helical mononuclear  $\text{Ln}^{\text{III}}$  building block, this unsymmetrical tridentate receptor has been incorporated into the segmental ligand  $\text{L}^5$  which is expected to produce self-organized triple-helical non-covalent lanthanide podates  $[\text{LnM}(\text{L}^5)_3]^{5+}$ , where  $\text{M}^{\text{II}}$  is a d-block metal ion occupying the facial pseudo-octahedral site produced by the three wrapped bidentate units, thus organizing the strands for their coordination to  $\text{Ln}^{\text{III}}$  [7].  $[\text{LnM}(\text{L}^5)_3]^{5+}$  are indeed selectively produced by the self-assembly processes, and various d-block

metals have been introduced to induce new electronic and structural properties in the final  $\text{Ln}^{\text{III}}$  devices (Fig. 2).  $[\text{EuZn}(\text{L}^5)_3]^{5+}$  acts as an efficient and water-resistant UV  $\rightarrow$  vis light-converting device [7],  $[\text{LnFe}(\text{L}^5)_3]^{5+}$  exhibit subtle synergic effects between the two metallic sites leading to the fine tuning of the  $\text{Fe}^{\text{II}}$  spin-crossover parameters [8], and  $[\text{LnCo}(\text{L}^5)_3]^{6+}$  represent the first inert facial non-covalent podates obtained with  $\text{Ln}^{\text{III}}$  as templating agents [9].

These self-organized non-covalent lanthanide podates offer fascinating possibilities for the molecular and supramolecular programming of structural and electronic properties in  $\text{Ln}^{\text{III}}$  devices. They are currently investigated as prototypes for *i*) selective recognition of  $\text{Ln}^{\text{III}}$ , *ii*) directional vis  $\rightarrow$  vis light conversion, *iii*) coupled optical-magnetic switches, and *iv*) luminescent metallomesogens.

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- [1] C. Piguet, *Chimia* **1996**, *50*, 144; D. Parker, J.A. Gareth Williams, *J. Chem. Soc., Dalton Trans.* **1996**, 3613.
- [2] N. Sabbatini, M. Guardigli, J.-M. Lehn, *Coord. Chem. Rev.* **1993**, *123*, 201; V. Alexander, *Chem. Rev.* **1995**, *95*, 273.
- [3] D.E. Koshland, *Angew. Chem. Int. Ed.* **1994**, *33*, 2375.
- [4] P.A. Brayshaw, J.-C.G. Bünzli, P. Froidevaux, J.M. Harrowfield, Y. Kim, A.N. Sobolev, *Inorg. Chem.* **1995**, *34*, 2068; J.M. Harrowfield, Y. Kim, B.W. Skelton, A.H. White, *Aust. J. Chem.* **1995**, *48*, 8071, and refs. cited therein.
- [5] F. Renaud, C. Piguet, G. Bernardinelli, J.-C.G. Bünzli, G. Hopfgartner, *Chem. Eur. J.*, submitted.
- [6] C. Piguet, J.-C.G. Bünzli, G. Bernardinelli, C.G. Bochet, P. Froidevaux, *J. Chem. Soc., Dalton Trans.* **1995**, 83; S. Petoud, J.-C.G. Bünzli, K. Schenk, C. Piguet, F. Renaud, in preparation.
- [7] C. Piguet, G. Bernardinelli, J.-C.G. Bünzli, S. Petoud, G. Hopfgartner, *J. Chem. Soc., Chem. Commun.* **1995**, 2575; C. Piguet, J.-C.G. Bünzli, G. Bernardinelli, G. Hopfgartner, S. Petoud, O. Schaad, *J. Am. Chem. Soc.* **1996**, *118*, 6681.
- [8] C. Piguet, E. Rivara-Minten, G. Bernardinelli, J.-C.G. Bünzli, G. Hopfgartner, *J. Chem. Soc., Dalton Trans.* **1997**, 421.
- [9] S. Rigault, C. Piguet, G. Hopfgartner, unpublished results.

## 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

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I spent my university years at the ETH-Zürich, studying chemistry at the 'Abteilung für Naturwissenschaften' from 1984 to 1988. Having obtained my diploma, I joined the group of Prof. Albert Eschenmoser. During my doctorate, I contributed to the total synthesis of sugar phosphates, a project which was carried out in the context of the question, how biomolecules could

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have emerged abiotically. After having obtained my Ph.D. in February 1993, I continued working for my former supervisor, starting the new, still ongoing project, in which the synthesis, pairing properties, and replication of pyranosyl-RNA ('p-RNA'), an isomer of RNA, were investigated. In February 1995, I moved to San Diego and worked for eight months at the 'Scripps Institution for Oceanography' in the group of Prof. Gustaf Arrhenius. This geochemist explores the structure and synthesis of double-layered metal hydroxide minerals, naturally occurring anion-exchange materials. We studied the interaction of such minerals, containing incorporated sulfite anions, with aldehydes and developed a mineral-assisted synthesis of sugar phosphates under very mild reaction conditions. In October 1995, I returned to the ETH-Zürich and joined the group of Prof. Andrea Vasella, who generously had accepted me as 'Habilitation'. Since October 1996, I have profited from the 'Alfred-Werner-Stipendium zur Förderung des akademischen Nachwuchses'.