Coordinatively Unsaturated Lanthanide(III) Helicates: Luminescence Sensors for Adenosine Monophosphate in Aqueous Media

Jashobanta Sahoo, Rajendran Arunachalam, Palani S. Subramanian,* Eringathodi Suresh, Arto Valkonen, Kari Rissanen, and Markus Albrecht*

Abstract: *Coordinatively unsaturated double-stranded helicates $[(H_2L)_2Eu_2(NO_3)_2(H_2O)_4](NO_3)_4$, $[(H_2L)_2Tb_2(H_2O)_6]$-$(NO_3)_6$, and $[(H_2L)_2Tb_2(H_2O)_6]Cl_6$ ($H_2L = butanedioicacid-1,4-bis[2-(2-pyridinylmethylene)hydrazide]$) are easily obtained by self-assembly from the ligand and the corresponding lanthanide(III) salts. The complexes are characterized by X-ray crystallography showing the helical arrangement of the ligands. Co-ligands at the metal ions can be easily substituted by appropriate anions. A specific luminescence response of AMP in presence of ADP, ATP, and other anions is observed. Specificity is assigned to the perfect size match of AMP to bridge the two metal centers and to replace quenching co-ligands in the coordination sphere.*

*I*n 1987 J.-M. Lehn introduced the term helicate for oligonuclear coordination compounds with two or more linear ligands wrapping around two or more metal ions.[1] This marked the beginning of intensive studies of helical metal complexes. Early on the interest mainly arose from mechanistic aspects.[2]

In the early investigations of helicates, properties and function played only a minor role. An exception was the pioneering work of Piguet and Bünzli on lanthanide helicates, which focused on some special features, such as photophysics or magnetism.[3,4] Nowadays, more and more helicates are used as structurally well-defined entities to interact with biochemical or biological systems.[5]

Nucleoside phosphates are the building blocks of DNA, a double-helical species found in nature. They themselves are unique species, which regulate the energy conversion in organisms. Furthermore, adenosine triphosphate (ATP), adenosine diphosphate (ADP), or adenosine monophosphate (AMP) play a key role in many cellular functions, for example

transport across membranes, DNA synthesis, or cell signaling.[6] Adenosine monophosphate (AMP) controls important processes in the regulation of carbohydrate metabolism, including glycogen phosphorylase and phosphofructokinase.[7]

Surprisingly, probes for the sensing of AMP (especially in the presence of ADP and ATP) are rare.[8] Odashima and co-workers[9] and Shao's group[10] had reported electrochemical detection methods. Fluorescent nano-silica sandwich complexes by Qu and co-workers[11] and a Cu complex by Lin[12] were reported. A guanidinium-based tweezer type receptor has been reported by Schmuck et al.[13] and a pyridinium-based tripodal chemosensor by Ghosh and co-workers.[14] The preferential binding order of receptors generally follows ATP > ADP > AMP, owing to the decreasing charge–charge interaction.

The present study introduces highly charged luminescent cationic lanthanide helicates to selectively recognize the less-charged AMP over ADP and ATP. Although various organo-fluorophores[15] were reported for sensing of AMP, most of these fluorophores bind generally through the phosphate terminals. In the present case, the receptor favors a bridging of AMP by involving both terminal moieties of the phosphate and the adenosine coordinating to the two metal centers. The receptor itself is a novel kind of luminescent coordinatively unsaturated double-stranded dinuclear helicate formed from two bis(tridentate) ligands H_2L (Figure 1) and two europium-(III) or terbium(III) ions. The coordination sites at the metal ions are filled up by water molecules or anions. Those co-ligands in principle can be substituted by anionic species. However, a thorough screening of possible anionic co-ligands for the helicate revealed that only AMP results in a significant change of the luminescent properties.

Ligand H_2L was prepared by reaction of succinic acid dihydrazide with 2-pyridine carboxaldehyde. Treating H_2L with $Eu(NO_3)_3$, $TbCl_3$, and $Tb(NO_3)_3$ results in the respective dinuclear Ln^{III} complexes $[Eu_2(H_2L)_2(NO_3)_2(H_2O)_4](NO_3)_4$,
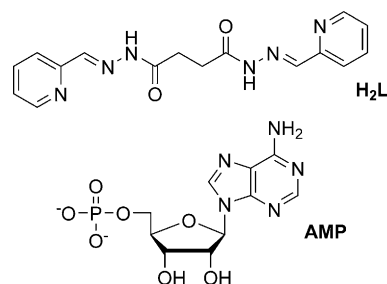
[*] J. Sahoo, R. Arunachalam, Dr. P. S. Subramanian, Dr. E. Suresh
Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Academy of Scientific and Innovative Research (AcSIR)
Bhavnagar, 364002, Gujarat (India)
E-mail: siva140@yahoo.co.in

Dr. A. Valkonen, Prof. Dr. K. Rissanen
University of Jyvaskyla, Department of Chemistry
Nanoscience Center
P.O. Box 35, 40014 University of Jyvaskyla (Finland)

Prof. Dr. M. Albrecht
Institut für Organische Chemie, RWTH Aachen University
Landoltweg 1, 52074 Aachen (Germany)
E-mail: markus.albrecht@oc.rwth-aachen.de

Figure 1. Ligand H_2L and AMP.

[Tb$_2$(H$_2$L)$_2$(H$_2$O)$_6$]Cl$_6$, and [Tb$_2$(H$_2$L)$_2$(H$_2$O)$_6$](NO$_3$)$_6$ (Supporting Information, S1–S9). Colorless crystals of the coordination compounds were obtained via slow diffusion of diethyl ether into methanolic solutions. The molecular structures confirm the formation of dinuclear double-stranded helicates as depicted in Figure 2.
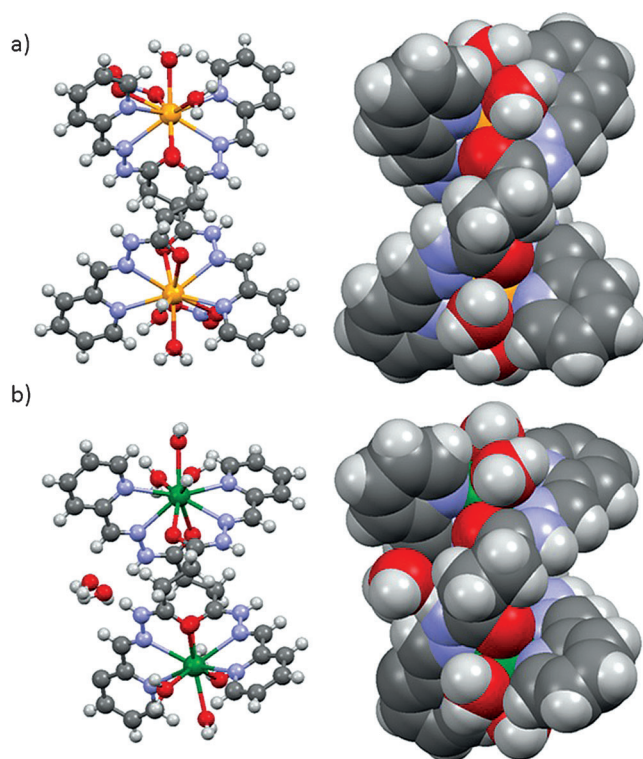

Figure 2. Structures of the cationic helicates [Eu$_2$(H$_2$L)$_2$(H$_2$O)$_4$(NO$_3$)$_2$]$^{4+}$ and [Tb$_2$(H$_2$L)$_2$(H$_2$O)$_6$]$^{6+}$ as observed in the crystal (C gray, H white, O red, N blue, Eu orange, Tb green).[22]

In the crystal structure, the europium(III) complex exists as discrete [Eu$_2$(H$_2$L)$_2$(NO$_3$)$_2$(H$_2$O)$_4$]$^{4+}$ ion (Figure 2 a) with four nitrates as counter ions and water as solvent of crystallization. [Eu$_2$(H$_2$L)$_2$(NO$_3$)$_2$(H$_2$O)$_4$](NO$_3$)$_4$ crystallizes in the orthorhombic space group *Aba*2. The cation possesses two symmetrically disposed ligand strands H$_2$L helically wrapping around the Eu···Eu axis with an intermetallic M···M distance of 8.013(6) Å. Each Eu^{3+} ion shows a coordination number of CN = 10. Among them, six sites are occupied by the N$_2$O chelates of two tridentate pyridyl acylhydrazone moieties of opposite ligand strands, two sites are occupied by a chelating nitrate anion, and two further sites are filled by two water molecules. Eu–O and Eu–N bond lengths are in the range of 2.401(2)–2.678(4) Å and 2.552(3) to 2.680(4) Å, respectively. The helical twist is reflected in the torsion angles at the central −C−C− bond of the spacer (82.8° and 74.08° respectively), which links the two pyridyl acylhydrazone moieties. An approximate orthogonal orientation (82.8° and 76.2° respectively) is observed in the mean planes of the metal chelated moieties of the ligand strands.

[Tb$_2$(H$_2$L)$_2$(H$_2$O)$_6$]Cl$_6$ (Figure 2 b) crystallizes in the monoclinic space group *P*2$_1$/*n*, while crystals of [Tb$_2$(H$_2$L)$_2$-

(H$_2$O)$_6$](NO$_3$)$_6$ were obtained in *P*$\bar{1}$. Those complexes are structurally similar to the corresponding europium compound with Tb···Tb distances of 7.577(5) or 7.8525(3)/7.7866(3) Å, respectively.

Both [Eu$_2$(H$_2$L)$_2$(NO$_3$)$_2$(H$_2$O)$_4$]$^{4+}$ and [Tb$_2$(H$_2$L)$_2$-(H$_2$O)$_6$]$^{6+}$ are luminescent in solid and solution state, showing typical emission of the corresponding lanthanide ion. To understand the effect of pH on the photophysics, the change in the luminescence intensity of [Eu$_2$(H$_2$L)$_2$(NO$_3$)$_2$(H$_2$O)$_4$]-(NO$_3$)$_4$ at 614 nm was monitored in water by varying the pH from 2–11 (Supporting Information, S11). The maximum emission intensity was observed in the pH range 7–9, matching well with the physiological pH. This encouraged us to use the complexes in sensing studies with anionic species. We realized that effects of additives on the photophysical properties of [Eu$_2$(H$_2$L)$_2$(NO$_3$)$_2$(H$_2$O)$_4$]$^{4+}$ are stronger than for [Tb$_2$(H$_2$L)$_2$(H$_2$O)$_6$]$^{6+}$. Based on this, we focused on the europium(III) complex.

In a preliminary screening experiment, different anions (100 equiv) were added to [Eu$_2$(H$_2$L)$_2$(NO$_3$)$_2$(H$_2$O)$_4$](NO$_3$)$_4$ in aqueous HEPES buffer (10 mм, pH 7.4). As anionic species F$^-$, Cl$^-$, Br$^-$, I$^-$, SO$_4$$^{2-}$, HSO$_4$$^-$, B$_4O_7$$^{2-}$, AcO$^-$, CO$_3$$^{2-}$, HCO$_3$$^-$, NO$_2$$^-$, NO$_3$$^-$, H$_2PO_4$$^-$, HPO$_4$$^{2-}$, PO$_4$$^{3-}$, AMP, ADP, and ATP were added as sodium salts. The corresponding luminescent responses are presented in Figure 3. Only AMP induces a significant luminescence change which is not observed with the other anions (even ATP, ADP, or the phosphates PO$_4$$^{3-}$, HPO$_4$$^{2-}$, and H$_2PO_4$$^-$). Addition of AMP to [Eu$_2$(H$_2$L)$_2$(NO$_3$)$_2$(H$_2$O)$_4$](NO$_3$)$_4$ enhances the quantum yield of the emission at 614 nm from Φ_{obs} = 1.8 % to Φ_{obs} = 6.1 % with an 64-fold enhancement of the emission intensity. The remarkable discrimination of AMP from ADP, ATP, and other inorganic phosphates PO$_4$$^{3-}$, HPO$_4$$^{2-}$, and H$_2PO_4$$^-$ (Figure 3, inset) by the luminescence change can be even observed by naked eye under an UV lamp (λ_{ex} = 320 nm). Competition experiments show that the emission intensity of the [Eu$_2$(H$_2$L)$_2$(NO$_3$)$_2$(H$_2$O)$_4$](NO$_3$)$_4$/AMP mixture is not
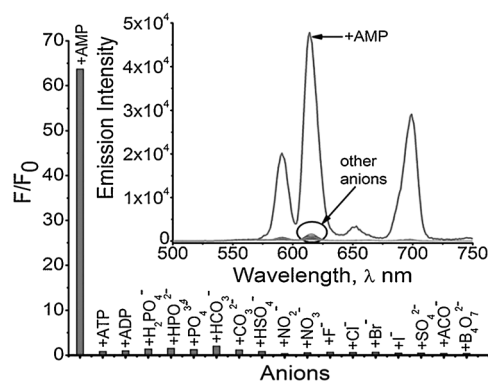
Figure 3. The luminescence response of [Eu$_2$(H$_2$L)$_2$(NO$_3$)$_2$(H$_2$O)$_4$]-(NO$_3$)$_4$ upon addition of various anions in HEPES buffer (10 mм, pH 7.4) upon excitation at λ_{ex} = 320 nm. The plot shows the relative luminescence intensity (F/F_0) of [Eu$_2$(H$_2$L)$_2$(NO$_3$)$_2$(H$_2$O)$_4$](NO$_3$)$_4$ (2 × 10^{-5} м) at 614 nm (F_0) against the emission upon addition of 100 equiv. of different anions (F). Inset: Corresponding luminescence spectra of [Eu$_2$(H$_2$L)$_2$(NO$_3$)$_2$(H$_2$O)$_4$](NO$_3$)$_4$ (2 × 10^{-5} м) in the presence of various analytes (100 equiv).

significantly affected by addition of other anions (Supporting Information, S12).

For a detailed evaluation of the binding interaction between AMP and $[Eu_2(H_2L)_2(NO_3)_2(H_2O)_4](NO_3)_4$, a systematic titration study was performed by varying the concentration of AMP from 0.1 equiv to 10 equiv (Figure 4), monitoring the emission bands at 592, 614, and 699 nm. All peaks show systematic luminescence enhancement.
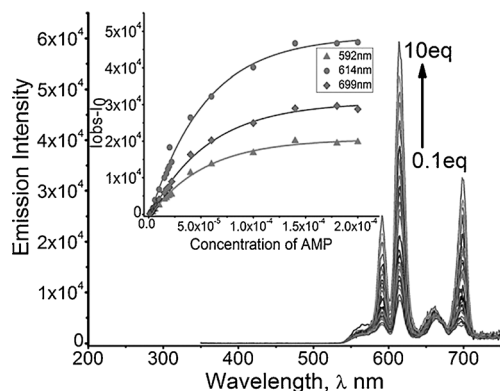

Figure 4. Evolution of the Eu^{III}-centered emission upon titration of $[Eu_2(H_2L)_2(NO_3)_2(H_2O)_4](NO_3)_4$ (2×10^{-5} M) with AMP in HEPES buffer (10 mM, pH 7.4) at $\lambda_{ex} = 320$ nm, showing the switching-on of emission. Inset: binding isotherms at 592 nm, 614 nm and 699 nm (I_{obs} is the observed emission intensity and I_0 is the initial emission intensity before adding AMP).

The Benesi–Hildebrand Equation (1)[16] (with F_0 and F being the luminescent intensities before and after addition of AMP; A is the concentration of AMP) enables the determination of the binding constant K_a.

$$\frac{1}{F-F_0} = \frac{1}{\kappa_a(F_{max}-F_0)[A^-]^n} + \frac{1}{F_{max}-F_0} \qquad (1)$$

By applying this equation for $[Eu_2(H_2L)_2(NO_3)_2(H_2O)_4]$-$(NO_3)_4$ with increasing concentration of AMP, a linear fit is obtained for $(1/F-F_0)$ versus $1/[AMP]$, revealing a 1:1 species to be present. A binding constant of $\log K_a = 3.83 \pm 0.01$ is estimated (Figure 5a). The 1:1 stoichiometry was also confirmed by Job's method of continuous variation (Figure 5b). A 1:1 mixture of $Eu_2(H_2L)_2$ and AMP shows in the positive

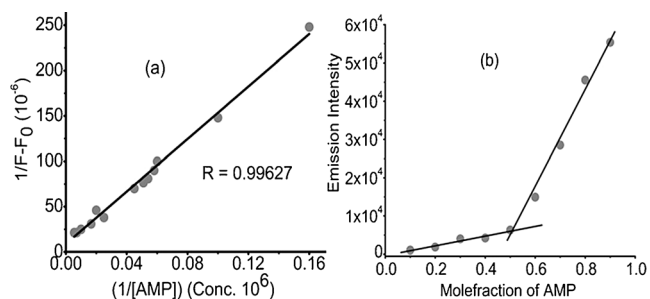**Figure 5.** Determination of K_a for the interaction of $[Eu_2(H_2L)_2(NO_3)_2$-$(H_2O)_4](NO_3)_4$ with AMP by the Benesi–Hildebrand method (a) and the corresponding Job plot (b), confirming the 1:1 stoichiometry.

ion HRMS spectrum at $m/z = 1294.1309$ the peak of $[(H_2L-2H)_2Eu_2-AMP]H^+$ (calcd: $m/z = 1294.1320$, S13). ESI-MS analysis shows that the imide group of the ligand can be deprotonated for charge compensation.[17]

In the absence of AMP, the luminescence intensity of $[Eu_2(H_2L)_2(NO_3)_2(H_2O)_4](NO_3)_4$ is relatively weak. The coordinated labile water at the Eu^{III} center is responsible for the observed low quantum yield (Φ) of $[Eu_2(H_2L)_2(NO_3)_2$-$(H_2O)_4](NO_3)_4$. Upon treatment with AMP, emission enhancement of up to 64-fold is induced by coordination of AMP and simultaneous displacement of the quenching water. The detection limit for AMP has been determined by standard techniques[18] to be 2 μM.

A recent report of Tan et al.[19] describes a coordination polymer made up of Eu^{3+} with AMP and used it for sensing of tetracycline (Tc) and citrate (Cit), respectively. Interestingly, the non-luminescent Eu-AMP polymer reported in the study becomes luminescent upon binding of Tc or/and Cit as lanthanide sensitizers. In contrast, the present $Eu_2(H_2L)_2$ double helicate already bears sensitizing units in the bridging ligand and thus switches from low luminescence to a 64-fold luminescence intensity upon binding of AMP. Thus AMP itself is not a sensitizer, owing to the low lying triplet level of AMP, which is lower than the resonance level of $^5D_0$ at Eu^{3+}.

The binding of one AMP to a double-stranded helicate should proceed as shown in Scheme 1. The phosphate unit coordinates to one of the europium(III) ions displacing water molecules and co-ligands. Now AMP is predisposed for a second binding through its imidazole-type unit of adenosine
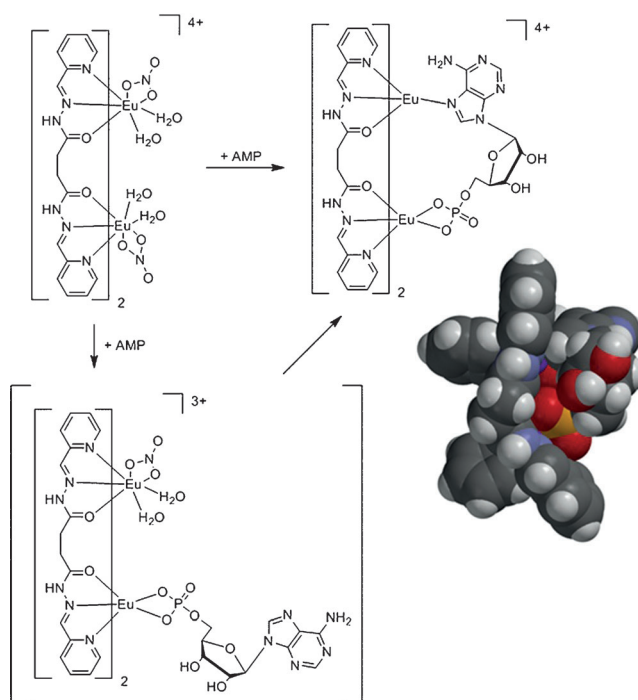
Scheme 1. Binding of AMP to a double-stranded helicate, which leads to displacement of water molecules. Force-field calculations[20] reveal that binding of AMP is only possible if the homochiral double-stranded helicate undergoes a transition into a hetero-chiral triple-stranded complex with the metal complex units possessing opposite configuration (see inset: computed force field model of $[(H_2L)_2Eu_2(AMP)]^{4+}$).

to the second metal center. However, to do this, the homochiral double-stranded helicate has to transform into a heterochiral species with side-on binding of the two ligands H_2L as well as AMP. Owing to its "banana-type" shape, the latter is already preorganized for this kind of binding. In this arrangement the coordination sites at the metal centers are sterically crowded leading to removal of water molecules. This enables the observed luminescence increase. For a model of a possible structure generated by force field calculations[20] see the structure presented in Scheme 1. Similar lanthanide bridging by AMP has already been observed.[21] Furthermore, the lifetime determined for a neat $[Eu_2(H_2L)_2(NO_3)_2(H_2O)_4]$-$(NO_3)_4$ complex and 1:1 ratio of Eu-complex/AMP mixture in aqueous medium provides $\tau = 0.14$ ms ($\kappa^2 = 1.055$) and 0.32 ms ($\kappa^2 = 1.085$). The enhancement in the lifetime from complex to AMP complex reflects an increment in their quantum yield, which further indicates the displacement of water quenchers upon binding of AMP.

In our experiments, we cannot detect the binding of ADP or ATP to the complex. However, we cannot rule it out. Modeling of an bridging ADP or ATP complex with a chelating internal phosphate unit reveals that the attached phosphate or diphosphate moiety sterically interacts with the bridging ligand L leading to the destabilization of the complex (Supporting Information, S14). This gives a tentative explanation for the AMP specific behavior of $[Eu_2L_2]^{6+}$.

In conclusion, we have presented a new type of coordinatively unsaturated double-stranded helicate. The complexes show a specific luminescence response to AMP, which is assigned to the ability to coordinate simultaneously to both metal centers in the dinuclear helicate. By this the number of quenching co-ligands at the metal centers is decreased and the luminescence is significantly enhanced, even in water. The unusual selectivity towards AMP over highly charged ADP and ATP is illustrated by $[Eu_2(H_2L)_2$-$(NO_3)_2]^{4+}$. The formation of the $[Eu_2(H_2L)_2AMP]^{4+}$ complex demonstrates a unique conformational and charge–charge interaction between the $[(Eu_2(H_2L)_2(NO_3)_2]^{4+}$ helicate and the nucleotide AMP.

[1] J.-M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier, D. Moras, *Proc. Natl. Acad. Sci. USA* **1987**, *84*, 2565.

[2] Reviews: a) C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, *97*, 2005; b) M. Albrecht, *Chem. Rev.* **2001**, *101*, 3457; c) M. J. Hannon, L. Childs, *J. Supramol. Chem.* **2004**, *16*, 7; d) M. Albrecht, *Angew. Chem. Int. Ed.* **2005**, *44*, 6448; *Angew. Chem.* **2005**, *117*, 6606; e) *Metallofoldamers, Supramolecular Architectures from helicates to biomimetics* (Eds.: G. Maayan, M. Albrecht), Wiley, Chichester, **2013**.

[3] a) C. Piguet, J.-C. G. Bünzli, *Chem. Soc. Rev.* **1999**, *28*, 347; b) J.-C. G. Bünzli, C. Piguet, *Chem. Rev.* **2002**, *102*, 1897; c) J.-C. G. Bünzli, C. Piguet, *Chem. Soc. Rev.* **2005**, *34*, 1048; d) B. Bocquet, G. Bernardinelli, N. Ouali, F. Floquet, F. Renaud, G. Hopfgartner, C. Piguet, *Chem. Commun.* **2002**, 930; e) M. Elhabiri, R. Scopelliti, J.-C. G. Bünzli, C. Piguet, *J. Am. Chem. Soc.* **1999**, *121*, 10747; f) N. André, T. B. Jensen, R. Scopelliti, D. Imbert, M. Elhabiri, G. Hopfgartner, C. Piguet, J.-C. G. Bünzli, *Inorg. Chem.* **2004**, *43*, 515; g) S. Torelli, D. Imbert, M. Cantuel, G. Bernardinelli, S. Delahaye, A. Hauser, J.-C. G. Bünzli, C. Piguet, *Chem. Eur. J.* **2005**, *11*, 3228; h) C. Piguet, C. Edder, S. Rigault, G. Bernardinelli, J.-C. G. Bünzli, G. Hopfgartner, *J. Chem. Soc. Dalton Trans.* **2000**, 3999; i) D. Imbert, M. Cantuel, J.-C. G. Bünzli, G. Bernardinelli, C. Piguet, *J. Am. Chem. Soc.* **2003**, *125*, 15698.

[4] For other selected lanthanide helicates, see: a) J. J. Lessmann, W. D. Horrocks, *Inorg. Chem.* **2000**, *39*, 3114; b) A. P. Bassett, S. W. Magennis, P. B. Glover, D. J. Lewis, N. Spencer, S. Parsons, R. M. Williams, L. De Cola, Z. Pikramenou, *J. Am. Chem. Soc.* **2004**, *126*, 9413; c) M. Albrecht, S. Schmid, S. Dehn, C. Wickleder, S. Zhang, A. P. Bassett, Z. Pikramenou, R. Fröhlich, *New J. Chem.* **2007**, *31*, 1755; d) M. Albrecht, O. Osetska, R. Fröhlich, J.-C. G. Bünzli, A. Aebischer, F. Gumy, J. Hamacek, *J. Am. Chem. Soc.* **2007**, *129*, 14178; e) S. Comby, F. Stomeo, C. P. McCoy, T. Gunnlaugsson, *Helv. Chim. Acta* **2009**, *92*, 2461.

[5] a) M. J. Hannon, V. Moreno, M. J. Prieto, E. Moldrheim, E. Sletten, I. Meistermann, C. J. Isaac, K. J. Sanders, A. Rodger, *Angew. Chem. Int. Ed.* **2001**, *40*, 879; *Angew. Chem.* **2001**, *113*, 903; b) A. D. Faulkner, R. A. Kaner, Q. M. A. Abdallah, G. Clarkson, D. J. Fox, P. Gurnani, S. E. Howson, R. M. Phillips, D. I. Roper, D. H. Simpson, P. Scott, *Nat. Chem.* **2014**, *6*, 797.

[6] a) E. Gendaszewska-Darmach, M. Kucharska, *Purigenic Signalling* **2011**, *7*, 193; b) B. S. Khakh, G. Burnstock, *Sci. Am.* **2009**, *301*, 84; c) W. G. Junger, *Nat. Rev. Immunol.* **2011**, *11*, 201.

[7] a) E. Helmreich, C. F. Cori, *Proc. Natl. Acad. Sci. USA* **1964**, *61*, 131; b) T. E. Mansour, *J. Biol. Chem.* **1963**, *238*, 2285.

[8] a) M. C. Heffern, L. M. Matosziuk, T. J. Meade, *Chem. Rev.* **2014**, *114*, 4496; For ADP or ATP detection see b) F. Huang, G. Hao, F. Wu, G. Feng, *Analyst* **2015**, *140*, 5873; c) J. A. Aguilar, E. Garcia-Espaiia, J. A. Guerrero, S. V. Luis, J. M. Llinares, J. F. Miravet, J. A. Ramireza, C. Soriano, *J. Chem. Soc. Chem. Commun.* **1995**, 2237; d) S. Nadella, P. M. Selvakumar, E. Suresh, P. S. Subramanian, M. Albrecht, M. Giese, R. Fröhlich, *Chem. Eur. J.* **2012**, *18*, 16784; e) S. Nadella, J. Sahoo, P. S. Subramanian, A. Sahu, S. Mishra, M. Albrecht, *Chem. Eur. J.* **2014**, *20*, 6047; f) M. Zhang, W.-J. Ma, C.-T. He, L. Jiang, T.-B. Lu, *Inorg. Chem.* **2013**, *52*, 4873; g) Q.-C. Xu, H.-J. Lu, Z.-Q. Lu, M. Liu, Y.-J. Li, X.-F. Wang, Y. Zhanga, G.-W. Xing, *RSC Adv.* **2014**, *4*, 47788; h) P. Hu, S. Yang, G. Feng, *Org. Biomol. Chem.* **2014**, *12*, 3701; i) A. E. Hargrove, S. Nieto, T. Zhang, J. L. Sessler, E. V. Anslyn, *Chem. Rev.* **2011**, *111*, 6603; j) N. Busschaert, C. Caltagirone, W. V. Rossom, P. A. Gale, *Chem. Rev.* **2015**, *115*, 8038; for lanthanide helicates in DNA analysis and cell imaging see: k) B. Song, C. D. B. Vandevyver, E. Deiters, A.-S. Chauvin, I. Hemmila, J.-C. G. Bünzli, *Analyst* **2008**, *133*, 1749; l) V. Fernández-Moreira, B. Song, V. Sivagnanam, A.-S. Chauvin,

C. D. B. Vandevyver, M. Gijs, I. Hemmila, H.-A. Lehr, J.-C. G. Bünzli, *Analyst* **2010**, *135*, 42.

[9] Y. Hisamatsu, K. Hasada, F. Amano, Y. Tsubota, Y. Wasada-Tsutsui, N. Shirai, S.-I. Ikeda, K. Odashima, *Chem. Eur. J.* **2006**, *12*, 7733.

[10] L. Shen, Z. Chen, Y. Li, P. Jing, S. Xie, S. He, P. He, Y. Shao, *Chem. Commun.* **2007**, 2169.

[11] Y. Song, C. Zhao, J. Ren, X. Qu, *Chem. Commun.* **2009**, 1975.

[12] X.-F. Shang, H. Su, H. Lin, H.-K. Lin, *Inorg. Chem. Commun.* **2010**, *13*, 999.

[13] H. Y. Kuchelmeister, C. Schmuck, *Chem. Eur. J.* **2011**, *17*, 5311.

[14] K. Ghosh, S. S. Ali, A. R. Sarkar, A. Samadder, A. R. Khuda-Bukhsh, I. D. Petsalakisc, G. Theodorakopoulosc, *Org. Biomol. Chem.* **2013**, *11*, 5666.

[15] a) M. S. Han, D. H. Kim, *Bioorg. Med. Chem. Lett.* **2003**, *13*, 1079; b) J. González-García, S. Tomi, A. Lopera, L. Guijarro, I. Piantanida, E. García-España, *Org. Biomol. Chem.* **2015**, *13*, 1732; c) P. Arranz-Mascarós, C. Bazzicalupi, A. Bianchi, C. Giorgi, M. L. Godino-Salido, M. D. Gutiérrez-Valero, R. Lopez-Garzón, B. Valtancoli, *New J. Chem.* **2011**, *35*, 1883; d) H. Gao, M. Xi, X. Qi, M. Lu, T. Zhan, W. Sun, *J. Electroanal. Chem.* **2012**, *664*, 88; e) I. Piantanida, B. S. Palm, P. Cudic, M. Zinic, H.-J. Schneider, *Tetrahedron Lett.* **2001**, *42*, 6779; f) A. A. Putnam, E. Jankowsky, *J. Mol. Biol.* **2013**, *425*, 3839; g) N. Singh, D. O. Jang, *Tetrahedron Lett.* **2011**, *52*, 2608.

[16] H. A. Benesi, J. H. Hildebrand, *J. Am. Chem. Soc.* **1949**, *71*, 2703.

[17] D. Wu, P. Huang, Y. Shui, G. Wu, *Inorg. Chem. Commun.* **2013**, *29*, 205.

[18] a) M. Kumar, N. Kumar, V. Bhalla, *RSC Adv.* **2013**, *3*, 1097; b) D. K. Singha, S. Bhattacharya, P. Majee, S. K. Mondal, M. Kumar, P. Mahata, *J. Mater. Chem. A* **2014**, *2*, 20908; c) B. Gole, A. K. Bar, P. S. Mukherjee, *Chem. Eur. J.* **2014**, *20*, 2276.

[19] a) H. Tan, B. Liu, Y. Chen, *J. Phys. Chem. C* **2012**, *116*, 2292; b) H. Tan, C. Ma, Y. Song, F. Xu, S. Chen, L. Wang, *Biosens. Bioelectron.* **2013**, *50*, 447.

[20] Spartan Essential "08, Wavefunction Inc., Irvine, USA.

[21] a) C. Aimé, R. Nishiyabu, R. Gondo, K. Kaneko, N. Kimizuka, *Chem. Commun.* **2008**, 6534; b) R. Nishiyabu, N. Hashimoto, T. Cho, K. Watanabe, T. Yasunaga, A. Endo, K. Kaneko, T. Niidome, M. Murata, C. Adachi, *J. Am. Chem. Soc.* **2009**, *131*, 2151; c) R. Nishiyabu, C. Aime, R. Gondo, T. Noguchi, N. Kimizuka, *Angew. Chem. Int. Ed.* **2009**, *48*, 9465; *Angew. Chem.* **2009**, *121*, 9629; d) C. Aimé, R. Nishiyabu, R. Gondo, N. Kimizuka, *Chem. Eur. J.* **2010**, *16*, 3604; e) R. Nishiyabu, C. Aimé, R. Gondo, K. Kaneko, N. Kimizuka, *Chem. Commun.* **2010**, *46*, 4333.

[22] CCDC 1453996 ([Tb$_2$(H$_2$L)$_2$(H$_2$O)$_6$]Cl$_6$), 1453997 ([Eu$_2$(H$_2$L)$_2$-(H$_2$O)$_4$(NO$_3$)$_2$](NO$_3$)$_4$), and 1458068 ([Tb$_2$(H$_2$L)$_2$(H$_2$O)$_6$]-(NO$_3$)$_6$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.
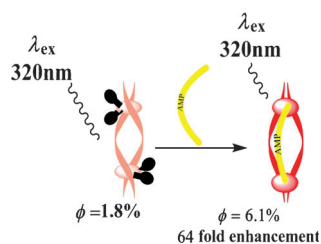
Communications

Luminescence Sensors

J. Sahoo, R. Arunachalam,
P. S. Subramanian,* E. Suresh,
A. Valkonen, K. Rissanen,
M. Albrecht* ———————— ■■■■–■■■■

Coordinatively Unsaturated
Lanthanide(III) Helicates: Luminescence
Sensors for Adenosine Monophosphate
in Aqueous Media

λ_{ex}
320nm

λ_{ex}
320nm

$\phi = 1.8\%$

$\phi = 6.1\%$
64 fold enhancement

One AMP is enough: A coordinatively unsaturated double-stranded dinuclear europium(III) helicate shows adenosine monophosphate (AMP)-specific luminescence response even in the presence of highly charged adenosine di- or triphosphate (ADP or ATP).

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