

NANOSCIENCE AND NANOTECHNOLOGY OF F ELEMENTS

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ABSTRACT

Medicaments that are carried via blood flow to sick organs; an electronic equipment capable of evaluating quality of beverages twice more sensitive than the human palate; magnets inside plastic micro-spheres that could help remove oil stains from the sea. Products that seem to have been taken from science fiction films, things that could never be part of our grandfather's imagination, they are actually the marvels of one more technological revolution: the nanotechnology. In this context, lanthanides and actinides elements play a fundamental role due to their singular chemical and physical properties. They appear as fundamental materials in a large range of areas such as, new materials applied to fuel element, sensors, electronics, drugs and markers (radio isotope), probes etc. The aim of this work is to review the chemistry and physics properties of these elements approaching this new technology point of view, emphasizing their nuclear applications.

1. INTRODUCTION

Nanotechnology is the creation and utilization of materials, devices, and systems through the control of matter on the nanometer-length scale—at the level of atoms, molecules, and supramolecular structures (Figure 1) [1-4]. The essence of nanotechnology is the ability to work at these levels to generate larger structures with fundamentally new properties and molecular organization. These “nanostructures,” made with building blocks based on first principles, are the smallest human-made objects and exhibit new physical, chemical, and biological properties and phenomena. Nanotechnology goal is to exploit these properties and efficiently manufacture and employ the structures. Nanotechnology has the potential to significantly impact environmental protection through understanding and control of emissions from a wide range of sources, development of new “green” technologies that minimize the production of undesirable byproducts, and remediation of existing waste sites and polluted water sources. Nanotechnology has the potential to remove the finest contaminants from water supplies and air as well as continuously measure and mitigate pollutants in the environment. Nanotechnology will revolutionize the biotech, medical, and pharmaceutical industries. This may reduce sickness and suffering and increase life expectancy. It is one of the most promising and exciting fields in science today. Figure 2 gives an expectative of nanotechnology in some branches of economy topics [5].

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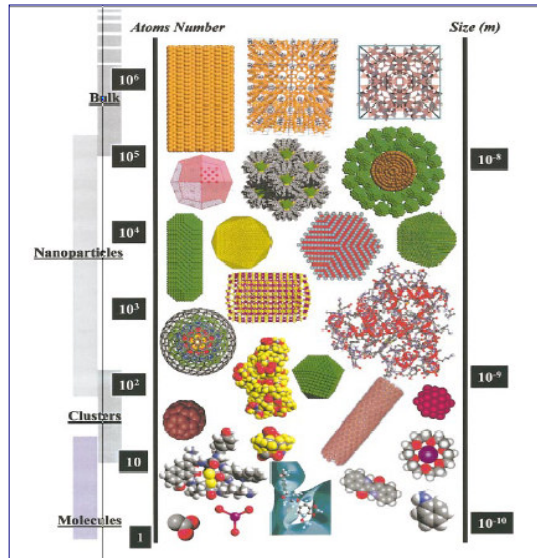


Figure 1. Exemplification of metric scale based on molecules and related materials (taken from reference 4).

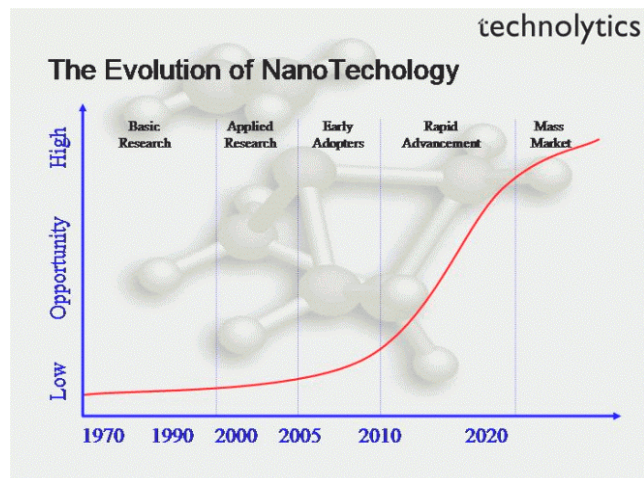
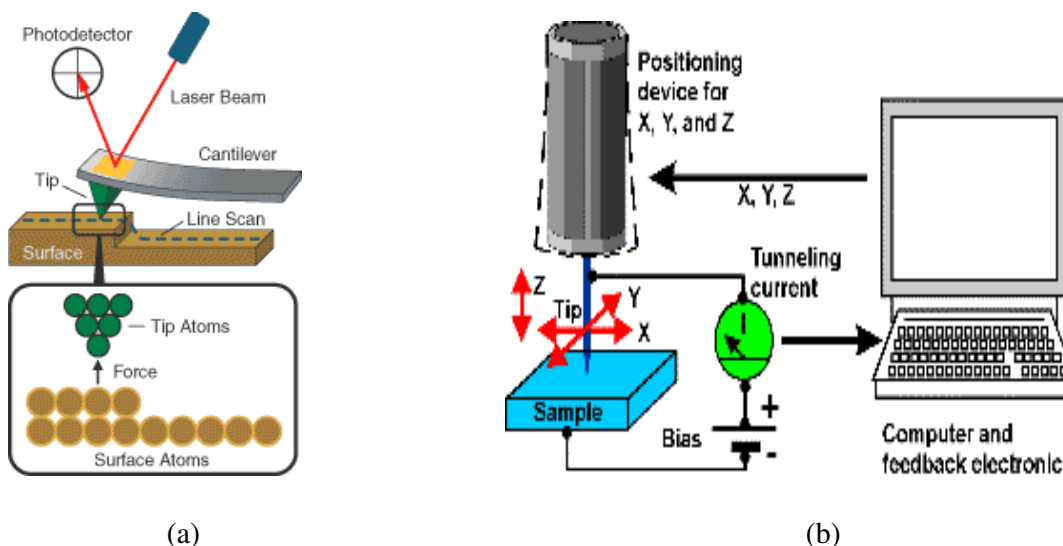


Figure 2. Expected development of nanotechnology [6].

Physicists have contributed with new tools of great promise for molecular engineering. These are *proximal probes*, including *scanning tunneling microscope* (STM) and *atomic force microscope* (AFM). A proximal-probe device places a sharp tip in proximity to a surface and uses it to probe (and sometimes modify) the surface and any molecules that may be stuck to it. These are the tools that really have contributed to the development of nanotechnology [3].

STM brings a sharp, electrically conducting needle up to an electrically-conducting surface, *almost* touching it. The needle and surface are electrically connected (Figure 3), so that a current will flow if they touch, like closing a switch. But just at what point soft, fuzzy atoms "touch"? It turns out that a detectable current flows when just two atoms are in tenuous contact-fuzzy fringes barely overlapping-one on the surface and one on the tip of the needle. By delicately maneuvering the needle around over the surface, keeping the current flowing at a tiny, constant rate, the STM can map shape the surface with great precision. Indeed, to keep current constant, the needle has to go up and down as it passes over individual atoms[1,3].

The related atomic force microscope (Figure 3) is even simpler in concept: A sharp probe is dragged over the surface, pressed down gently by a straight spring. The instrument senses motions in the spring (usually optically), and the spring moves up and down whenever the tip is dragged over an atom on the surface. The tip "feels" the surface just like a fingertip in the simulated molecular world [1,3].



(a) (b)
Figure 3. Schematic representation of AFM (a) and STM (b)[7,8].

2. THE LANTHANIDE AND ACTINIDE ELEMENTS

Lanthanides and actinides elements are known by their unusual properties especially by the spectroscopic, magnetic properties, hazardous and radioactivity, viewpoint.

Lanthanide complexes in OLEDs application. Electroluminescence is the conversion of electrical energy into light. Organic light emitting diodes (OLEDs) currently are being developed for flat panel display technologies with great success. However, problems with color purity and efficiencies of energy transfer still remain. The lanthanide complexes are used as emitting layers in OLEDs. Lanthanide-based luminescence is preferable to organic-based luminescence because of greatly increased color purity and its emission efficiency.

In the design of the lanthanide ion complexes researches goals are two main parts: 1) the development of complexes with geometry control 2) the development of antenna ligands that will absorb energy and transfer it efficiently to lanthanide ions.

There are two main advantages in manufacturing EL devices using rare earth complexes: (i) theoretically the upper limit of inner quantum efficiency is near 100%, which is four times higher than that for similar devices using other materials; and (ii) the sharp emission bands of rare earth ions is very suitable for full-color display. In particular, Eu^{3+} ions are known to be weakly fluorescent species due to their low quantum yields and poor molar absorption. The technique of ligand-sensitized fluorescence has been considered to be an efficient method for enhancing its fluorescence. In this method, an organic ligand with a higher molar absorption is complexed with the Eu^{3+} [9-19]. On excitation in its absorption band, the ligand transfers a part of its excitation energy to the higher energy levels of Eu^{3+} , which then emits light. Such an indirect way of excitation results in the fluorescence enhancement of Eu^{3+} compared to direct one. A number of organic ligands such as β -diketones, aromatic carboxylic acid or polymers have been used as sensitizing ligands for this purpose [13,17,18,19]. Generally, in EL devices using europium complexes the N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) is used as Hole Transport Layer (HTL), [10, 13, 15, 16]. PVK and NPB were also used in other devices [9 -14]. The design of these OLEDs are directly linked to a design of lanthanides LEMD. In Fig 4 it is presented a schematic OLED material.

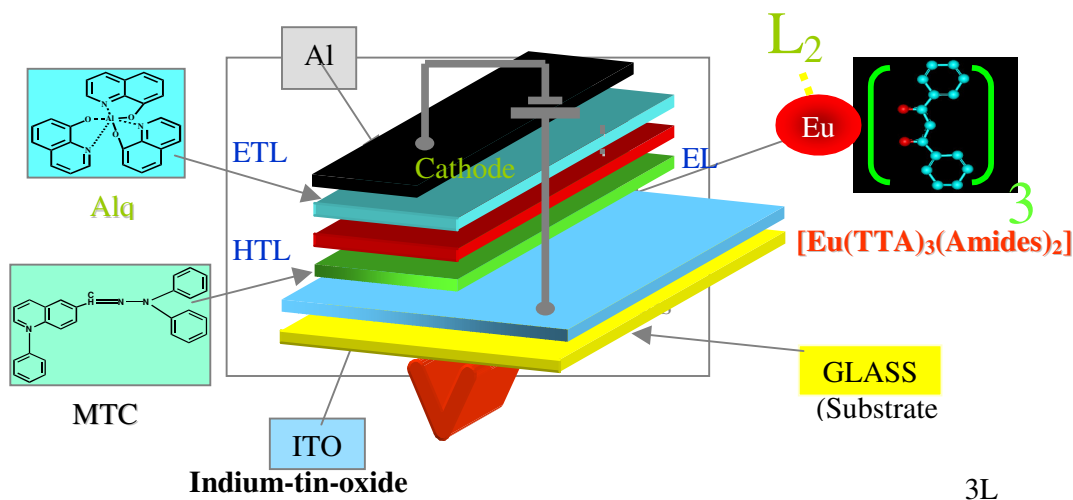


Figure 4.. OLEDs with Eu^{3+} -complexes as the Emitting Layer

Fluorescent properties of fluorescent lanthanide labels and time-resolved analysis. It is well known that Sm, Eu, Tb, and Dy ions emit fluorescence of specific wavelength when they coordinate to specific ligands. Compared to the traditional organic fluorescent materials, the lanthanide coordination compounds have the following properties: (1) Long lifetime. Lanthanide complexes, mainly of europium and terbium, have long fluorescent lifetimes longer than several hundreds microseconds, whereas traditional organic reagents have several nano seconds; (2) Large Stokes shift. In most case, the complexes are excited by UV absorption, and emit light of wavelength longer than 500 nm. The emission peaks of Eu, Sm, Tb, and Dy complexes are 615 nm, 643 nm, 545 nm, and 574 nm, respectively; (3) The fluorescent peak profiles are sharp: The half-widths are 10nm – 20 nm. It is known that the fluorescence is based on the energy-transfer from the ligand to the central metal ion. Using such fluorescent properties, time-resolved fluorescent immunoassays and DNA hybridization assays using lanthanide fluorescent complexes as a label have been developed. Time-resolved fluorometry has a potential to reduce various backgrounds of short lifetime, and enables highly sensitive detection. Fig 5 shows the principle of the time-resolved fluorescence homogeneous detection [20-25].

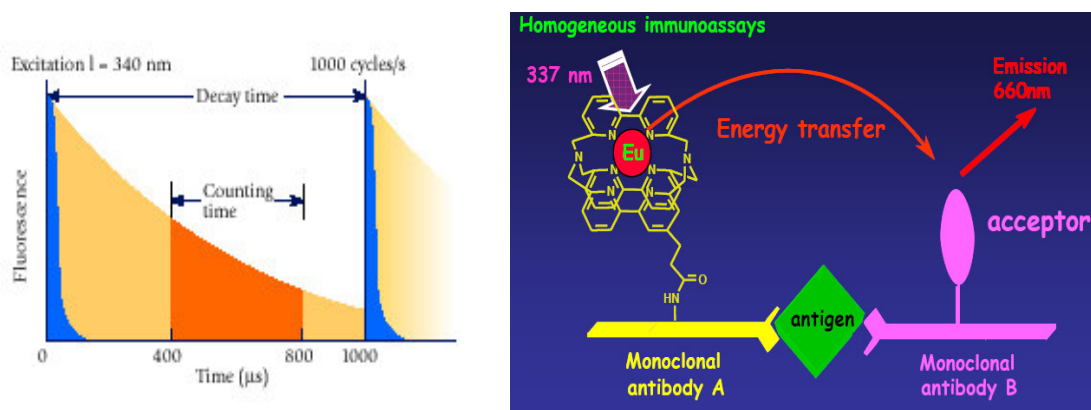


Figure 4.. Principle of the time-resolved fluorescence homogeneous detection

However, traditional time-resolved fluorescent immunoassays have not been effectively utilized, because direct labeling to biomaterials was impossible and weak fluorescence of the labels. Therefore, it was developed a new class of fluorescent labels as included BHHCT, a new europium ligand, criptands, calixarenes crown ether, etc, which has a potential to solve the problems of traditional systems (Fig 5). This ligand can form a stable complex with europium, and emits strong fluorescence, which is specific to europium after photo-excitation of the ligand. In addition, some of this ligand carries a chlorosulfonyl group, which enables direct labeling of biomaterials having amino groups [26-27].

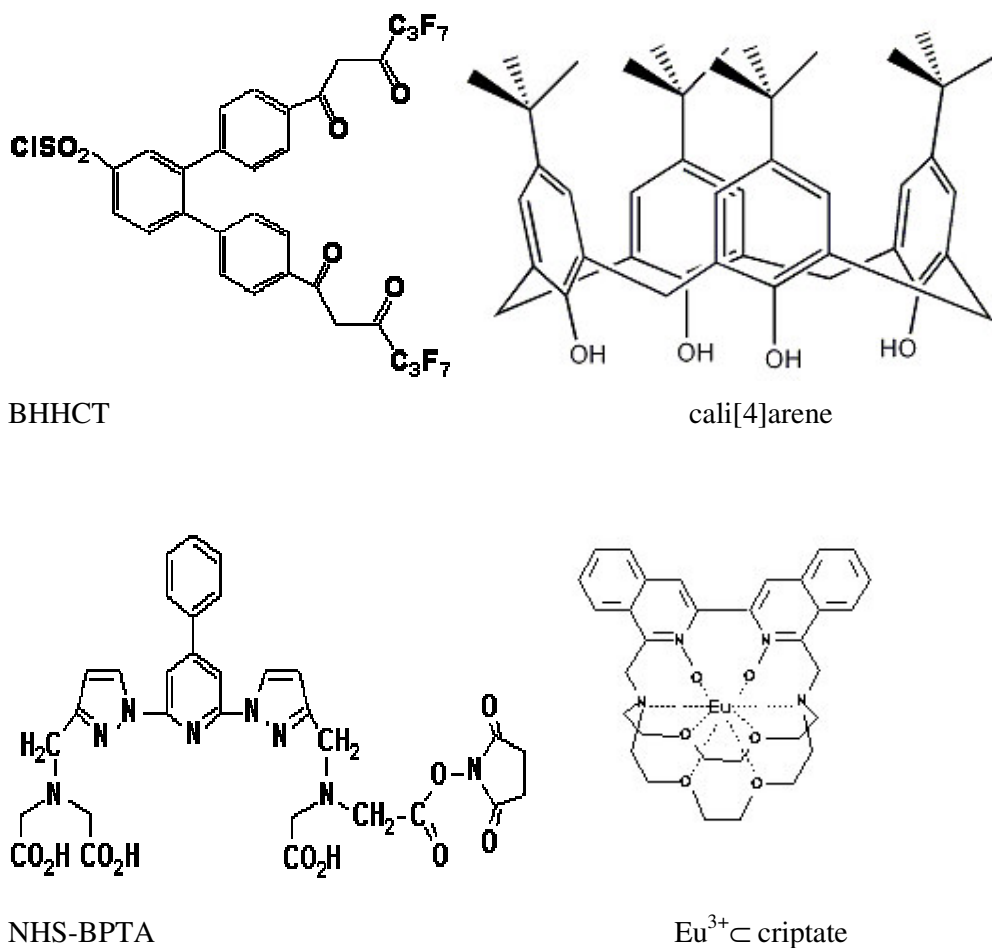


Figure 5.. Ligands and a criptate complex in fluoroimmunoassay

Lanthanide binding tags (LBTs) are the next generation of fluorescent tags. Since this one tag can potentially aid in protein purification, characterization, and structure determination, it could be a very important tool for proteomics research. LBTs are short polypeptides (15-25 amino acids) derived from calcium-binding motifs and modified to bind trivalent lanthanide ions with nM affinity. The goal is to establish stable complexes with physical properties that are useful in biochemical and biophysical investigations. Because the LBT tags are small, they have minimal impact on the structures and functions of proteins to which they are fused. Furthermore, because they are composed exclusively of amino acids, these tags can be fused to proteins of interest using standard molecular biology techniques. Preliminary studies suggest that the unique photophysical properties of LBTs lead them to applications in cell biology and biochemistry, providing information about the topology of multi-enzyme complexes, protein-protein interactions, and protein localization. In addition, LBTs facilitate NMR and X-ray crystallographic structure determination. The former is aided by the paramagnetic properties of the lanthanide ion, while the latter utilizes the strong scattering power of the metal. The excellent scattering properties of the bound lanthanide ions make

these tags ideal tools for crystallographic phasing of macromolecular structures. Currently, multi-wavelength anomalous dispersion (MAD) using selenomethionine (SeMet) a derivated protein that is the most rapid and efficient phasing method. While SeMet technology represents a real advance over the more traditional heavy atom methods, it has some significant drawbacks. First, selenium has fewer electrons than the heavier lanthanides, and so scatters X-rays less effectively and has a smaller anomalous signal[28]

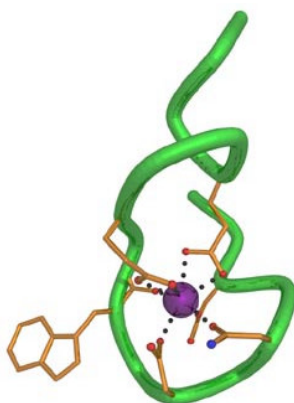


Figure 6 The structure of a tag where Tb^{3+} is liganded solely by the protein with no involvement of water molecules, which quench the fluorescence

2.2 THE ACTINIDES IN THE NANOWORLD

Of all actinides, U and Th are the elements most studied from the research viewpoint. They occur in natural form while the others are produced by irradiation. The principal area where nanotechnology will be more focused to these elements is in the energy area.

Nuclear fission. Despite its air of "political incorrectness" and the very real problems of nuclear waste disposal, nuclear fission remains a major contributor to the energy mix worldwide, contributing some 26×10^{18} J of electrical energy in 2000 [29]. Its contribution, moreover, will almost certainly increase in the next few years.

Uranium. All commercial power reactors use the isotope ^{235}U , which is fissionable by slow neutrons. As it is well known, it constitutes only ~0.7% of natural uranium, so fuel must be enriched in the fissionable isotope, a cumbersome and capital-intensive procedure.

Most natural uranium consists of isotope ^{238}U , which is not fissionable by slow neutrons. However, ^{238}U will absorb a slow neutron to yield ^{239}Pu after a chain of short-lived α -decays. Plutonium-239 is fissionable by slow neutrons. It has been extensively used in nuclear weapons but not for commercial power generation, both because of safety and nonproliferation concerns. Since Pu is an element, it can be separated from its environment by chemical means, and so making a concentration that would be usable in nuclear explosives is relatively simple. Enriching ^{235}U , on the other hand, requires isotopic separation, which is

considerably more difficult and at least heretofore has required an enormous infrastructure. Pu-fueled power reactors, however, have been thought likely to be necessary some day. Indeed, "mixed oxide" fuels, containing up to 5% Pu obtained from reprocessed spent uranium fuel, are already used in a few countries [29].

Thorium. A third nuclide of relevance for fission power is ^{232}Th , the only long-lived isotope ($t_{1/2} \sim 1010$ y) of thorium. Like ^{238}U , it is not fissionable by slow neutrons, but it will absorb a neutron to form ^{233}Th , which β -decays over several days to fissionable ^{233}U . Although there has been interest in thorium as an energy source for decades for many years the US Geological Survey had a "Branch of Uranium and Thorium Resources"— ^{233}U has not been employed on other than an experimental basis. Nonetheless it remains a "backstop" energy resource, particularly since the crustal abundance of Th (7.2 ppm) is about four times that of U [30].

Applications of nanotechnology to fission energy. Fission is obviously a thermal technology, and it's hard to see how it can be otherwise. The energies of nuclear reactions lie orders of magnitude above those of chemical bonds, so even molecularly structured assemblages seem unlikely to be able to control nuclear reactions at the atomic level. However, this does not mean MNT is irrelevant to fission. Most obviously, thermoelectric power generation may prove practical.

Mining and extraction. The big application of MNT towards fission fuels, however, probably lies in their extraction and separation. Fission fuels are "fossil," too, in a sense: they also are dug out of the Earth and their supply is ultimately finite. As described below, a major resource-related application of nanotechnology lies in the low energy molecular separation of elements, most directly from aqueous solution. For other elemental commodities, therefore, nanotechnology could vastly increase the supply of U and Th. Leaching of low-grade U- or Th-bearing rocks, for hydrometallurgical extraction, has already been carried out (e.g., Sayed et al., [31]), and selective "uranophiles" (highly selective agents for complexing the uranyl ion, UO_2^{2+}) have been the focus of many researches (Araki et al., [32]; Jacques & Desreux, [33]; Nagasaki & Shinkai, [34]; Shinkai et al., [35] 1989; Xu & Raymond, [36] 1999). Uranium also exists in natural brines; indeed, extraction of UO_2^{2+} from seawater has been investigated (Aihara et al. [37], 1992; Kanno, [38] 1981; Kelmers, [39] 1981; Yamashita et al., [40] 1981). A potential "down side" relevant to nuclear proliferation should be mentioned. Protactinium-231 ($t_{1/2} \sim 3 \times 10^4$ y), which occurs naturally in small amounts in uranium-bearing materials from the decay of ^{235}U , could also be extracted. This isotope is the only naturally occurring one besides ^{235}U with possible utility in a nuclear device (Franka, [41] 1994), and unlike ^{235}U it could be purified without the necessity of separating isotopes.

Reprocessing of nuclear fuel and separation of nuclear waste. The result of nuclear fission is a mishmash of fission products, the lighter nuclei formed by the fission of the U atoms, mixed together with a set of heavier U and actinide isotopes formed by absorption of stray neutrons.

The fission products tend to be strongly β -active because they are neutron-rich. The actinides are δ -active and typically long-lived on a human timescale (as with ^{239}Pu). A fair amount ($\sim 1\%$ ^{235}U , as well as $\sim 5\%$ Pu generated *in situ*; USDOE-EIA, [29]) of unreacted fuel also remains, but it is unusable because of competitive absorption of neutrons by the other nuclides.

Obviously, it would be attractive to separate the components of nuclear waste, for fuel recovery and also to recover potentially valuable radionuclides. However, separating "reprocessing" nuclear waste is both difficult and hazardous. Indeed, such complex mixtures are difficult to deal with even when not strongly radioactive. The procedures involve

dissolution in strong acid and then separation via a long and complicated sequence of steps using precipitation, ion exchange, solvent extraction, and so on, with the additional difficulty that all reagents and materials used themselves become contaminated with radioactive material.

Separation from such solutions could alternatively be carried out molecularly, by systems like those described in reference [42]. Indeed, besides the "uranophiles" described above, effort has been directed toward finding actinide-specific binding agents, although the focus of these studies has been therapeutic applications (e.g., Raymond et al., [43]; Kappel et al., [44]). This is a more difficult problem, however, because of radiation damage to the nanomechanisms. They will have to be robust and ultimately probably self-repairing. If such systems can be developed, they will make the reprocessing of nuclear waste considerably more practical. Indeed, possibly each reactor installation could reprocess its own waste.

Such technologies, however, will also have unfortunate political ramifications. They are likely to make it much easier for small groups to extract nuclear materials from radioactive waste such as that from conventional power reactors. Separation of elemental plutonium (or ^{233}U from irradiated thorium) should be relatively straightforward, even if the lifetimes of the nanomechanisms are limited due to radiation damages.

Applications of nanotechnology to fusion energy. Whether nanotechnological fabrication would significantly help the production of fusion reactors is unclear. Obviously, the same considerations of relative energy differences between the nuclear reactions vs. those of the chemical bonds in any confinement device apply just as strongly here as they do in the case of fission energy. Possibly, however, alternatives to the "brute-force" fusion by thermal plasmas, such as laser ignition or electrostatic confinement, will benefit from fabrication at nanoscale precision.

Separation of nuclear fuels. The obvious application of nanotechnology to fusion, as for fission, again lies in the cheap separation of nuclear materials. The nuclides proposed as most promising for fusion (e.g., ^7Li , ^{11}B) are all of rare elements. On a per-atom basis, B makes up 0.0019% of the crust; Li 0.0060% [42]. However, both have been enriched in certain natural brines, which would facilitate their separation by some known techniques described in ref [42].

Other nanomaterials based on uranyl ion as optical materials The uranyl-doped fluorophosphate glasses $75\text{NaPO}_3\text{-}24.5\text{SrF}_2\text{-}0.5\text{UO}_2\text{F}_2$ and $60\text{NaPO}_3\text{-}24.5\text{SrF}_2\text{-}15\text{LiF-}0.5\text{UO}_2\text{F}_2$ have been discussed in terms of optical absorption and luminescence spectra. The absorption spectrum of the uranyl ion in glasses shows less fine structure than the spectra of uranyl complexes in solution. The glass samples exhibit a strong luminescence typical for the uranyl ion, and the luminescence spectrum is well resolved. It was found that the force constant of the vibrations in the ground state is intermediate between that in fluoride and phosphate glasses. During the glass preparation, reduction of uranyl to tetravalent uranium is often observed.[45]

Distinct species U(III), U(IV), U(V) and U(VI) have been identified when U(VI) or U(IV) species are doped into the cubic elpasolite lattice. The band intensities, and derived vibrational frequencies, in the luminescence and absorption spectra of the uranyl ion situated in this lattice are compared with those of $\text{Cs}_2\text{UO}_2\text{Cl}_4$. In particular, the intensity enhancement of the $\text{B}_{2g} \rightarrow \text{A}_{1g}(\text{D}_{4h})$ hypersensitive transition shows that the uranyl ion occupies a major site of C_{2v} or lower symmetry[46].

Uranyl-Salophen Complexes as new receptors and catalysts Salophen ligands are diimino tetradentate dianionic ligands that form very strong complexes with the uranyl di cation UO_2 .

These complexes behave as electrically neutral, hard Lewis acids and are excellent receptors for anions and neutral molecules in lipophilic solvents. Structural modifications of the basic skeleton of the salophen ligand lead to the synthesis of efficient ditopic receptors for ions pair (i.e tetralkylammonium salts, alkali metal salts). Because of the large ionic radius of the uranium in the uranyl cation, the ligand cannot assume a planar geometry, but is highly puckered. This implies that non-symmetrically substituted uranyl-salophen derivatives exist in principle as a pair of enantiomers.[47] .

Homooxocalixarenes The chemistry of these oxygenated homologues of calixarenes is currently developed according to the following main lines: a) synthesis of new parent polyphenol compounds; b) complexation of uranyl and other metal ions by parent polyphenol ligands; c) synthesis of ether and ester derivatives of homooxocalixarenes with preorganized cavity for strong and selective complexation of organic, cations and neutral species; d) structural and conformational analysis of homooxocalixarenes; e) development of host-guest systems based on homooxocalixarene and related cyclophanes suitable for anchoring to solid surfaces[48-50].

The uranyl ion as a solar cells storage -The world conventional energy supplies, which are based mainly on readily available fossil fuel source, are diminishing rapidly. The main approach to the energy crisis, nuclear fission, is raising a great deal of hope but its practicality is yet to be demonstrated. There is no doubt that solar energy, which is clean and non-hazardous, could contribute considerably to a solution of the energy problem if appropriate methods were developed to collect, concentrate, store and convert solar radiation which is diffuse and intrinsically intermittent.

The operation of a Luminescent Solar Concentrators (LSC) is based on absorption of solar radiation in a collector containing a fluorescent species in which the emission bands have little or no overlap with the absorption bands. The luminescence spectra of uranyl ion present these characteristics . The fluorescence emission is trapped by total internal reflection and concentrated at the edges of the collector which is usually a thin glass plate.[42].

3. CONCLUSIONS

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Due to their special properties elements f (Ln and An) present a big potential as smart materials into the new era of nanotechnology and the nanotechnology will play a role in the next generations.

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REFERENCES

- 1 H. E. Toma, "O Mundo Nanométrico: a dimensão do novo século", Oficina de Textos, São Paulo, Brazil (2004). v. 1. 102 p.
- 2 J. Uldrich and D. Newberry, "The Next Big Thing Is Really Small: How Nanotechnology Will Change the Future of Your Business", Crown bisness , USA (2003)
- 3 E. Drexler, C. Peterson and G. Pergamit, "Unbounding the future: the nanotechnology revolution", N.Y. USA, 1991.
- 4 A. J. Green, Aust. J. Chemistry, **55**(3), pp.183-186 (2002).
- 5 R.A. Sá Ferreira, L. D. Carlos, V. de Zea Bermudez, "Luminescent Organic-Inorganic Nanohybrids", in Encyclopedia of Nanoscience and Nanotechnology, edited by H. S. Nalwa (American Scientific Publishers, North Lewis Way, California, USA (2004), Vol. 4, pp. 719-762.
- 6 **Extracted from web** http://www.directionsmag.com/images/articles/nano_tech/nano1.gif (2005)
- 7 **Extracted from web** http://www.molec.com/what_is_afm.html.2005
- 8 **Extracted from web** http://www.beugungsbild.de/stm/stm_basics.html (2005)
- 9 F.P Duclerc. J.R. Matos, H.F. Brito L.D. Carlos.. *J. Appl Polymer Sci* **83**(12). pp. 2716-2726 (2002).
- 10 R. Reyes, E.N. Hering, M. Cremona, C.F.B. Silva, H.F. Brito, C.A. Achete, *Thin Solid Films*, **420-421**, pp 23-29 (2002).
- 11 R. Reyes, C.F.B. da Silva, H.F. de Brito, and M. Cremona *Braz. J. Phys.*, **32**(2b), pp.535-539(2002).
- 12 K. Okada, Y. Wang, and T. Nakaya, *Synt. Metals*, **97**, pp. 113 (1998).
- 13 Y. Miyamoto, M. Uekawa, H. Ikeda, and K. Kaifu, *J. Lumin.* **81**, pp. 159 (1999).
- 14 C.J. Liang, Z.R. Hong, X.Y. Liu, D.X. Zhao, D.Z. Zhao, W.L. Li, J.B. Peng, J.Q. Yu, C.S. Lee, and S.T. Lee, *Thin Solid. Films*, **359**, pp. 14 (2000).
- 15 H. Cao, X. Gao, C. Huang, *Appl. Surface Sci.* **161**, pp. 443 (2000).
- 16 N. Takada, J. Peng, and N. Minami, *Synt. Metals*, **121**, pp. 1745 (2001).
- 17 H.F. Brito, O.L. Malta, and J.F.S. Menezes, *J. Alloys Comp*, **336**, pp 303 (2000).
- 18 O.L. Malta, H.F. Brito, J.F.S. Menezes, F.R. Gonçalves, S.A. Silva Jr, F.S. Farias, and A.M. de Andrade, *J. Lumin.* **75**, pp 255 (1997).
- 19 C. Liang, W. Li, Z. Hong, X. Liu, J. Peng, L. Liu, Z. Lu, M. Xie, Z. Liu, J. Yu, and D. Zhao, *Synt. Metals*, **91**, pp 151 (1997).
- 20 J.-C.G. Bünzli, G.R. Choppin (Eds.), *Lanthanide Probes in Life, Chemical and Earth Sciences: Theory and Practice*, Elsevier, Amsterdam, (1989).
- 21 R. Saez & P A.Caro, *Rare Earths*, Ed. Complutense, Madri, Espanha, (1998).
- 22 JL Toner, "Inclusion Phenomena and Molecular Recognition", In: JL Atwood (ed), "*Lanthanide chelates as luminescent probes*", Plenum Press: NY London, ,pp 185-197(1990).
- 23 I. Hemmilä, T. Stahlberg and P. Mottran *Bioanalytical Applications of labeling technologies Immunoassays*, Wallac Turku, (1994).
- 24 L. Thunus and R. Lejeune, *Coord.Chem. Rev.*, **184**, pp. 125-155, (1999).
- 25 J. Yuan, G. Wang, K. Majima and K. Matsumoto, , *Anal. Chem.*, **73**, pp1869-1876 (2001).
- 26 T. Nojima, Y. Kondoh, S. Takenaka, T. Ichihara, M. Takagi, H. Tashiro and K. Matsumoto, *Nucleic Acids Res. Supplement*, **1**, pp105-106 (2001).

- 27 W. T. Maso, *Fluorescent and Luminescent Probes for Biological Activity*, Academic Press, N.Y., (1999) 647p.
- 28 USDOE-EIA, United States Department of Energy—Energy Information Agency, (2000).Online at www.eia.doe.gov.
- 29 Mason, B; Moore, C B.; *Principles of Geochemistry*, 4th Ed., John Wiley & Sons, (1982).
- 30 S. A.Sayed, T. M.; Sami, Abaid, A. R., *Sep. Sci. Technol.*, **32**, pp 2069, (1997)
- 31 Araki, K; Hashimoto, N; Otsuka, H; Nagasaki, T; Shinkai, S; *Chem.Lett.*, **5**, pp 829-832, (1993).
- 32 J. Vincent; J.F. Desreux, *Inorg. Chem.*, **35**, pp.7205-7210 (1996).
- 33 T. Nagasaki and S. Shinkai, *Perkin Trans.* **2**, pp1063-1066, (1991).
- 34 S. Shinkai, Y. Shiramama, H. Satoh, O. Manabe, T. Arimura, K. Fujimoto, T. Matsuda, *Perkin Trans.* **2**, pp. 1167-1171, (1989).
- 35 J. Xu and K.N. Raymond; *Inorg. Chem.*, **38**, 308,(1999).
- 36 T. Aihara, A. Goto, T. Kago, K. Kusakabe and S. Morooka, *Sep. Sci. Technol.*, **27**(12), pp. 1655, (1992).
- 37 M. Kanno *Sep. Sci. Technol.*, **16**, pp.999-1017,(1981).
- 38 A. D. Kelmers, *Sep. Sci. Technol.*, **16**, pp. 1019-1035,(1981).
- 39 H. Yamashita, K. Fujita,F. Nakajima, Y. Ozawa, T. Murata, *Sep. Sci. Technol.*, **16**, pp. 987-98, (1981).
- 40 J. Franka, *Letter, Physics Today*, **47**, pp.84, (1994).
- 41 S.L. Gillett, *Nanotechnology: Clean Energy and Resources for the future*, Foresight Institute, University of Nevada, NV,USA (2002).
- 42 K. N. Raymond, G. E.Freeman, M.J. Kappel, *Inorg. Chim. Acta*, **94**, pp.193-204, (1984).
- 43 M. J. Kappel, H Nitsche and K. N. Raymond, *Inorg. Chem.*, **24**, pp. 605-11, (1985).
- 44 H De Leebeek, C Görller-Walrand and J L Adam, *J. Phys. Condens. Matter* **11**(21), pp. 4283-4287(1999).
- 45 P A Tanner, C. S K Mak, Z. Pei, Y Liu and L Jun *J. Phys.: Condens. Matter* **13**(1) pp 189-194(2001).
- 46 M Cametti, M Nissinen, A Dalla Cort and L. Mandolini *J Am Chem Soc*, **127**,pp 3831 - 3837 (2005).
- 47 B. Masci and P. Thuéry *Polyhedron*, **24**, pp 229 - 237(2005).
- 48 B. Masci and P. Thuéry . *New J Chem*, **29**, pp 493 - 498(2005) .
- 49 G. Doddi, G. Ercolani, P. Mencarelli and A Piermattei *J. Org. Chem*, **70**, pp 3761 - 3764 (2005) .