GOBIERNO DE ESPAÑA · MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Convocatoria de ayudas a PROYECTOS
EXPLORA « CIENCIA » y EXPLORA « TECNOLOGÍA »
2013

El programa EXPLORA trata de promover la curiosidad científica y la osadía intelectual en investigación fundamental y aplicada. Este programa busca propuestas de investigación imaginativas y radicales cuya viabilidad científica pudiera ser considerada baja en programas convencionales, porque chocan con ideas ortodoxas en su campo, y también con propuestas tecnológicas arriesgadas, que buscan una prueba de concepto, y que en ambos casos no se conseguirían financiar por las vías habituales.
A diferencia de otros, en el programa EXPLORA no es prioritaria la búsqueda del éxito de la propuesta, ya que más que avances en el conocimiento científico o humanístico se busca indagar nichos intelectuales que puedan llevar a descubrimientos radicales y también a decepciones. El programa EXPLORA está abierto a cualquier investigación honesta y seria de la frontera del conocimiento. Las propuestas al programa EXPLORA podrán ser de índole teórica o experimental.

Antes de solicitar un proyecto EXPLORA lea la siguiente información:

- Solo se puede solicitar un proyecto EXPLORA en esta convocatoria, la modalidad entre Explora Ciencia y Explora Tecnología la dará la orientación del proyecto solicitado.
- La heterodoxia y la radicalidad intelectual es la esencia del programa EXPLORA. El lema de este programa es: "*ATRÉVETE A DESCUBRIR. ATRÉVETE A EQUIVOCARTE*".
- Los proyectos EXPLORA han sido diseñados para financiar solamente la fase de exploración de la bondad de ideas heterodoxas y radicalmente innovadoras.
- Que una propuesta sea interdisciplinaria o transdisciplinaria no significa que sea heterodoxa y/o radical. EXPLORA no busca proyectos necesariamente interdisciplinarios o transdisciplinarios, sino propuestas intelectualmente arriesgadas. Tampoco un proyecto de temática rara o inusual, es necesariamente una buena propuesta EXPLORA.
- Si usted considera que su proyecto es excelente, si está seguro que un buen experto en su campo lo evaluaría positivamente (en una convocatoria convencional), entonces NO es el tipo de propuesta que busca EXPLORA.
- El programa EXPLORA es muy competitivo, con un porcentaje de propuestas seleccionadas menor del 15 %. La mayor parte de las propuestas rechazadas en la convocatoria EXPLORA son buenos o excelentes proyectos que debieran ser financiados por otros programas de investigación autonómicos, nacionales o europeos convencionales. Las solicitudes presentadas al programa EXPLORA serán valoradas por una comisión técnica en la que participará un panel de expertos seleccionados atendiendo a la naturaleza y finalidad de los proyectos Explora « Ciencia » y Explora « Tecnología » y formado por científicos y humanistas elegidos por su solvencia profesional pero también por su vasta cultura científica y/o por el carácter interdisciplinar o transdisciplinar de su investigación..
- En la memoria técnica se deberá exponer claramente:
  - El marco conceptual o experimental del problema que desea estudiar.
  - Su propuesta alternativa, subrayando donde reside la novedad radical de la misma.
  - El impacto científico y socio-económico que podría tener su idea.
  - Los investigadores o investigadoras que participarán en el estudio y el papel que jugarán en el mismo.
  - Los principales puntos fuertes pero también los principales puntos débiles de su propuesta, es decir porqué en un programa convencional no le aprobarían su propuesta.

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INSTRUCCIONES PARA COMPLETAR LA MEMORIA CIENTÍFICO-TÉCNICA DE PROYECTOS DE I+D DEL SUBPROGRAMA DE GENERACIÓN DE CONOCIMIENTO (PROGRAMA ESTATAL DE FOMENTO DE LA INVESTIGACIÓN CIENTÍFICA Y TÉCNICA DE EXCELENCIA)

Lea detenidamente estas instrucciones para completar correctamente la memoria-científico técnica.

1. Este modelo de memoria está restringido en su extensión máxima y por consiguiente ha de limitarse a los espacios indicados al completarla.
2. Las memorias pueden completarse en español o en inglés, a excepción del apartado 1. RESUMEN DE LA PROPUESTA, que debe completarse en ambos idiomas.
3. Se recomienda completar la memoria empleando un pc con sistema operativo Windows y usando como procesador de textos MS Word (MS Office).
4. Para completar los textos, sitúe el cursor en las zonas sombreadas. 4000 caracteres son, aproximadamente, una página.
5. Una vez terminada la memoria, guarde su archivo en formato pdf (de no más de 4Mb) y apórtelo a la solicitud telemática del proyecto en el apartado “Añadir documentos”.
6. Debido a que este formulario está diseñado para incluir únicamente texto con un tipo de letra determinado, si necesita incluir fórmulas, reacciones químicas, fórmulas matemáticas, etc., o figuras aclarativas, deberá hacerlo en los anexos I y II, respectivamente, tras citarlas en el cuerpo del texto. No deberá emplear más extensión que la indicada.
7. El formulario está adaptado para poder emplear la opción de “copiar y pegar”.

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AVISO IMPORTANTE

En virtud del artículo 11 de la convocatoria **NO SE ACEPTARÁN NI SERÁN SUBSANABLES MEMORIAS CIENTÍFICO-TÉCNICAS** que no se presenten en este formato.

1. RESUMEN DE LA PROPUESTA / SUMMARY OF THE PROPOSAL

(Debe rellenarse también en inglés / It should also be completed in English)

INVESTIGADOR PRINCIPAL (Nombre y apellidos):

José Lorenzo Alonso Gómez

TÍTULO DEL PROYECTO:

Estructuras Quirales Inteligentes para el control e inhibición de la Corrosión

ACRÓNIMO:

SmartCFCorr

PALABRAS CLAVE
Máximo 100 caracteres
Corrosión– Recubrimientos– Respuestas quirópticas – Sensórica – Autoensamblaje – Síntesis – STM

TITLE OF THE PROJECT:

Smart Chiral Frameworks to Control and Inhibit Corrosion

ACRONYM:

SmartCFCorr

KEY WORDS
Maximum 100 characters
Corrosion – Coatings–Chirotical responses – Sensing – Self-assembly – Synthesis – STM

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RESUMEN

Máximo 2000 caracteres

La corrosión supone un porcentaje importante del PIB mundial. En materiales, la durabilidad y la apariencia a largo plazo están directamente relacionadas con la protección de estos frente a la corrosión. El método de protección más utilizado frente a la corrosión es mediante recubrimientos orgánicos que aíslen el material del medio, pero existen dos grandes problemas: a) la evaluación del grado de recubrimiento suministrado por la capa de imprimación, que condicionará el comportamiento futuro de la pintura y, b) la detección precoz de la corrosión, que permita adoptar medidas preventivas. La tecnología actual más fiable para realizar ambas tareas se basa en medidas de intensidad de corriente que atraviesa el recubrimiento. La gran desventaja de estas técnicas es la dificultad de correlacionar la corriente global medida con el área específica de corrosión de la pieza estudiada. En el caso de la obras de arte, someter la pieza a corrosión inducida para diagnosticar su grado de protección conlleva una desventaja inaceptable.

Con el presente proyecto pretendemos desarrollar Estructuras Quirales Inteligentes (EQI) para la protección de materiales contra la Corrosión de dos formas. La primera es el uso de EQI para formar capas monomoleculares mediante autoensamblaje para la protección frente a la corrosión. Estas capas ultrafinas permitirán una protección invisible al ojo humano pero visible a las espectroscopías quirópticas, permitiendo de esta manera asegurar una protección completa de la superficie sin necesidad de someter a las pieza a protejer a tests agresivos (Fig. 5, annexe II). La segunda, dado que los procesos de corrosión llevan asociados una modificación del pH del medio, proponemos incorporar EQI en las imprimaciones convencionales. Estas EQI con propiedades quirópticas record son sensibles al pH, por lo que mediante escaneado de la superficie se podrán mapear los puntos de iniciación de corrosión de una forma precisa y precoz (Fig. 5, annexe II).

SUMMARY

Maximum 2000 characters

Corrosion is a significant percentage of world GDP. In materials, durability and long-term stable appearance are directly related to protection against corrosion. The method most widely used is protection by organic coatings that isolate the material from its environment. In this area, two major problems still remain without an optimal solution. One is the evaluation of the degree of coverage provided by the primer coating, which will determine the future behavior of the paint. Furthermore, early detection of the onset of corrosion, allowing preventive measures and reduction of costs, is still a challenge. Currently the most reliable technology performs these tasks based on measurements of electrical current through the coating. The major disadvantage of these techniques is the difficulty of correlating the overall current measured with the specific area affected by corrosion of the studied system. In the case of metallic artworks, submitting the piece to induced corrosion in order to diagnose the degree of protection involves unacceptable damage to the masterpieces.

With this project we aim at developing Smart Chiral Frameworks (SCFs) for the protection of materials against corrosion in two ways: I) Construction of Smart Chiral Monolayers (SCMs) by self-assembly of SCFs. These ultrathin layers allow protection invisible for the human eye but detectable with chiroptical spectroscopies, thus allowing to ensure complete surface protection without subjecting the sample to aggressive tests (Fig. 5, anexo II). II) Since corrosion processes are associated with a change in the pH of the medium, we propose to incorporate Smart Chiral pH Sensors (SCpHSs) for Corrosion Mapping in conventional primers. These SCpHSs with chiroptical responses sensitive to pH for scanning the surface of the protected objects with chiroptical spectroscopies may detect and map corrosion initiation sites at an early stage accurately (Fig. 6, anexo II).

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1.- Proyecto EXPLORA

Máximo 18000 caracteres

Exponga de forma breve pero clara los siguientes aspectos de la propuesta:

- el problema que desea estudiar
- el marco conceptual o experimental del problema en la actualidad
- su propuesta alternativa, subrayando dónde reside su novedad radical
- las actividades a desarrollar para validar su idea

THE PROBLEM

Chemical reactions of metals with the environment are responsable for corrosion. In this context, the primary protection method is isolation of the material to be protected, which is usually done by organic coatings. Organic coatings applied on metallic substrates usually comprise of several coats, as depicted in Fig. 1 (annexe II). Each coat is designed for a specific functionality (UV protection, barrier, inhibition or color), and for good performance of the whole coating system a key property needs to be met, which is chemical compatibility between the coatings, as well as between the first level and the substrate, guaranteeing good adherence between coatings and between the whole system and the substrate.

The first level, named primer or base coating, is complex because from one side it will provide covalent bonding (if possible) with the (metallic or ceramic) substrate, and from the opposite side it will be able to form supramolecular interactions, as strong as possible, with the subsequent organic layer.

The base coating should be as thin as possible, ideally one monolayer, to minimize energy changes due to stress associated to the different thermal coefficients of the (metallic or ceramic) substrate and the organic layer on top, which tend to produce disbanding. The solutions currently in the market meet more or less this criterion, with thicknesses below one micrometer. The great challenge is, however, how to verify the degree of coverage of a nanometer thick layer either for stand-alone application (single layer for art objects exposed in museums) or for base coating (case of industrial application: automotive, ships, and aircrafts). The only solution available nowadays is testing the whole coating system a posteriori, for adherence (good coverage of the primer layer) and/or corrosion resistance as a unit. Therefore, at the moment it is not possible to map the defects in order to localize them on the surface.

Although the stand-alone application is of minor importance in terms of surface treatment compared with industrial applications, the relevance for preservation of cultural heritage is very high, especially in European countries, which are very rich in museums. The function of those institutions is to safely display the cultural heritage. This is not an easy task because of the degradation caused by the exposure to the environment.

CURRENT PROTECTION AGAINST CORROSION

At the metal−coating interface, where the primer coating lies, the effort nowadays is finding substitutes for the highly efficient chromate conversion coatings that have been prohibited due to environmental issues. Alternate layers should be able to provide similar protection. The current attempts are based on sol−gel technologies, but there is still a long way ahead. Moreover, real-time monitoring of the primer coating for a priori assessment of the quality of the final performance of the coating system is still a must. No solutions are currently available to verify on real time, during the painting process, the degree of coverage of a nanometer-thick primer.

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Concerning the bulk of the system, the development of coating functionalities able to sense pH changes is a new open area. pH changes towards acidic in anodic areas and towards alkaline in cathodic sites are directly related to the early development of the corrosion process (Fig. 2, annexe II). Recent developments in the corrosion initiation process by visual or light inspection involve the inclusion of nano-containers in the coating, i.e. nanoparticles loaded with pH indicators.[1] This solution allows early detection of the corrosion process, but decreases the efficiency of the coating itself. Clearly, further developments are necessary prior to reaching an stage of applicability.

NOVEL PROTECTION AGAINST CORROSION

An object non-superimposable with its mirror image is chiral. This property is widely present in Nature, where most biomolecules are chiral. The interacion of chiral molecules with polarized light result in optical rotatory dispersion (ORD) and circular dichroism (CD).[2] Due to the high sensitivity of these chiroptical spectroscopies to molecular geometry and supramolecular interactions, they are very often crucial in configurational assingment as well as in the characterization of complexes.[3] In materials with inherent chirality, chiroptical response alterations can be employed for imaging.[4] In order to obtain efficient materials for those applications, systems with very strong chiroptical responses are desired. As mentioned earlier, CD and ORD are very sensitive to the geometry of the molecules, and therefore in order to avoid cancelation of responses from different conformations, systems with a defined geometry are desired. In a meticulous design to control the transition electric and magnetic dipole moments (responsable of the chiroptical responses),[2] we have prepared a shape-persistent macrocycle with the strongest CD response for organic compounds to date.[5] The purelly alleno-acetylenic linear oligomers also present outstanding CD outputs.[6] Incorporation of functionalities into these systems allows them to function as sensors. Recently, we have prepared a pyridine cyclophane[7] sensitive to pH in a reversible manner (Fig. 3, annexe II).

Chiral amplification can be achived by going from individual to collective chirality.[8] As an example, we have used a chiral platform to anchor achiral nanoparticles resulting in exceptionally large chiral amplifications.[9] Motivated by these results, we studied the self-assembly of chiral pyridoallenes on surfaces. In collaboration with the research group of Prof. Barth at the Technical University of Munich, where scanning tunnling microscopy (STM) studies were performed, we have developed the construction of up-standing chiral architectures (UCAs) from enantiopure allenes (Fig. 4, annexe II). As demonstrated by a combination of molecular dynamic simulations (MDs), ESI-MS, and tip manipulations, the topological self-assembly of the molecules was found to have a crucial role in the formation of these novel chiral surfaces. Careful analysis of high resolution STM images confirmed the transfer of chirality from single molecules to the 2D networks. (Manuscript in preparation) The use of enantiopure allenes with strong chiroptical responses along with their up-standing organization opens great possibilities for the construction of new smart sensing and imaging materials.

I.- Smart Chiral Monolayers (SCMs) for Corrosion Protection

We propose the design, synthesis, and self-assembly of Smart Chiral Frameworks (SCFs) to function as protecting groups against metallic surface corrosion and also as sensors for the onset of such corrosion. These SCFs are composed of three parts:

1. Anchoring THIOL for covalent linkage to the surface

2. Signaling CHIRAL moiety to enable mapping of the monolayers through chiroptical responses

3. Protecting SILANE for corrosion protection (and adhesion to many paint systems if extra layers are required)

With our recent results in UCAs in hand, we aim at building novel UCAs for the construction of stable Smart Chiral Monolayers (Fig. 5 annexe II). Therefore, we propose the incorporation of an anchoring thiol (1) to gain sufficient stability for industrial usage. As mentioned above, incorporation of chiral moieties (2) may provide these molecules with outstanding chiroptical responses. Additionally, their self-assembly into UCAs could lead to chiral amplification improving the imaging. Finally, silane (3) incorporation will provide anode and cathode inhibition over the protected surface to preclude corrosion.

II.-Smart Chiral pH Sensors (SCpHSs) for Corrosion Mapping

We propose to design, synthesis, and incorporate in paints organic macrocycles bearing:

1. Anchoring Groups for adhesion to paints
2. Signaling CHIRAL moiety to enable mapping
3. Proton RECEPTOR

We have vast experience in the construction of chiral macrocycles with remarkable chiroptical responses. More importantly, we incorporated functional groups enabling those macrocycles to sense pH changes via chiroptical spectroscopies. Now we want to go one step further and implement them into conventional paints to serve as early mapping of corrosion (Fig. 6 annexe II). These SCpHSs should bear anchoring groups in order to properly adhere to paints (1), chiral elements to provide the resulting macrocycle with strong chiroptical responses (2), and a proton receptor (3) that will induce sensing of the pH through ORD and CD.

HOW TO PROCEED

I.-Smart Chiral Monolayers (SCMs) for Corrosion Protection

a) Design of Smart Chiral Frameworks:

We have recently introduced the use of chiral allenes for the constructions of Up-standing Chiral Architectures and demonstrated that the novel tectons form highly-ordered, dense-packed superstructures following topological self-assembly principles. The rotation of the terminal allene-di-tert-butylethylene moieties (colored in Scheme 1 annexe I) around the alkyne axis together with the bending of the alkyne axis results in extremely large conformational freedom. Importantly, significant chiroptical activity is evidenced by the CD spectra despite averaging over all possible molecular conformations and orientations present in solution. The gas phase properties of 1 were investigated with electrospray ionization mass spectroscopy (ESI-MS), where a tendency to form dimers was detected. For a better understanding of the strong dimerization tendency, we performed systematic molecular dynamics (MD) simulations with MMFF.[10] The most likely conformation adopted by 1 to form the dimers (Fig. 4 annexe II) is characterized by antiparallel-oriented pyridine centers and complementarily-packed allene groups inducing the impression of hugging molecules. Interestingly, the hug at the top (arbitrarily chosen, large y in Figure 1d) of the dimer is different from the one at the bottom (small y) probably due to the 120º angle between positions 2 and 6 of the pyridine ring.

The monolayers formed by 1 are not stable above 200 K. We will explore different ways to improve this stability (Scheme 2 anexo I), such as incorporating an anchoring thiol group in R1 to have covalent linkage to the metal substrate. The incorporation of a silane group as R2 will complete the funtionality of the SCMs for corrosion protection (A). The incorporation of carboxylic functional groups in the molecule will open the possibility for stronger intermolecular

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interactions as well as polymerizing the SCMs (B). In this way, light-induced covalent cross-linking seems possible allowing a polymerization after the monolayer coating has been applied to the targeted object. On the other hand, in order to improve the topological self-assembly of these systems, a 2,5-disubstituted pyridine nucleous will be used instead of a 2,6-disubstituted pyridine, as in 1 (C).

b) Synthesis of the Smart Chiral Frameworks (SMFs)

On one hand, the preparation of A and C has been planned following described procedures in our research group that involve the cross-coupling reaction between 2,6- or 2,5-dibromopyridene with 1,3-di-tert-butyldiethynylallene.[7] On the other hand, compound B will be prepared using the same procedure but starting with 2,6-dibromopyridine-4-carboxylic acid. The presence of the extra substituent at the 4 position opens ways to further derivatize the system conveniently.

c) Scanning tunneling microscopy (STM)

Investigation of the self-assembly, anchoring and cross-linking potential of the employed chiral species will be carried out on model systems under well-defined conditions, more specifically on single-crystal metal surfaces in ultra-high vacuum. The Prof. Barth and Priv.-Doz. F. Klappenberger have contributed significantly to the so-called STM+XS approach providing a comprehensive characterization of 2D nanoarchitectures with complementary surface sensistive techniques, namely STM and X-ray spectroscopy. This approach allows for a detailed investigation of the assembly behavior in the submonolayer and monolayer regime on the single-molecule level. X-Ray photoelectron spectroscopy is highly sensitive to the chemical state of the molecules, its changes induced by the assembly process or temperature treatment as well as to the signatures of surface anchoring. Furthermore, the orientation and conformation of the organic units can be assessed with near-edge adsorption-fine-structure spectroscopy. An operational low- and variable-temperature STM apparatus is available in the laboratory in Munich and F. Klappenberger has agreed to contribute measurement time to the project. Beamtime at the BESSY synchrotron for high-resolution XPS and NEXAFS experiments can be applied for and is very likely to be granted due to the long-lasting collaboration with Prof. Wöll (KIT, Karlsruhe, Germany). The findings of the model system investigation will allow to evaluate the processes underlying the monolayer formation and thus to optimize the design of the organic species with respect to improved stability and chiroptical response of the final chiral architecture in a closed feedback loop together with the structure of the Smart Chiral Frameworks employed.

d) Chiroptical responses of Smart Chiral Monolayers (SCMs)

Nowadays, the formation of self-assembled monolayers (SAM) is well explored.[11] Once we have in hand SCMs of good stability, we will form the SCMs onto a substrate transparent to the UV-Vis light in order to measure the ORD and CD properties of the monolayers.[12] The measured results compared with the chiroptical responses in solution will give information about the chiral amplification caused by the self-assembly. These results will drive towards SCMs with strong chiroptical responses.

e) Corrosion tests

The formation of self-assembled monolayers, SAMs, will be done in the usual way by dipping process,[13,14] although alternate ways, such as spraying or vapor deposition, will also be explored in the Dept. of Chemical Engineering at the University of Vigo in collaboration with Prof. X. R. Nóvoa.

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The kinetics of SAM formation will be followed by electrochemical quartz crystal microbalance and/or electrochemical capacitance determinations.[15] The corrosion inhibition properties will be evaluated using electrochemical impedance spectroscopy at the macro- and microscales.[16]

II) Smart Chiral pH Sensors (SCpHSs) for Corrosion Mapping

a) Design of Smart Chiral pH Sensors (SCpHSs)

As mentioned above, we have a chiral pyrido-allenophane with CD signals sensing pH (Fig. 3, annexe II). However, this system senses only very acid conditions. With the aim of using SCpHSs for early corrosion detection we will incorporate proton receptors more sensitive to pH. We have used in the past years allenes as que chiral moieties, however this chiral entity photoisomerizes when donating groups are present in the molecule.[17] Last year in collaboration to Central Soulth University (China) we got funded (2013) a project to develop spirane chiral moieties. This project has been funded (2014) by Emerxentes (Xunta de Galicia) and soon will provide the first chiral macrocycles. Therefore, and since some of the proton receptors are electron donating groups, we will incorporate also spiranes as chiral moieties. Incorporation of an ester group in the periphery will allow to post synthetic modification for tuning the mixability to different paints.

b) Synthesis of Smart Chiral pH Sensors (SCpHSs)

For the last years, we have been dealing with the preparation of different shape-persistent chiral allenoacetylenic macrocycles using inter- and intramolecular approaches. Both strategies include palladium cross-coupling and/or oxidative acetylenic homocoupling reactions as key steps along with intercalated protection and deprotection reactions of the corresponding functional groups. Full characterization of the resulting compounds has been achieved by the combination of different spectroscopic techniques with theoretical computations and X-ray diffraction.

The present project comprises the preparation of new chiral acetylenic macrocycles with high variability regarding the proton receptor (green moieties in Scheme 3 annexe I) and the chiral motif (blue moieties in Scheme 3 annexe I) with the aim of tailoring the properties that would furnish the final compounds with pH-mapping capabilities. We plan to use the same strategies as those already described starting from dihaloheteroaromatic compounds, most of them commercially available, which would undergo Sonogashira cross-coupling reactions with the chiral unit bearing the acetylenic moieties. The synthesis of the latter has already been developed in our research group at the University of Vigo.

c) pH Sensitivity of Smart Chiral pH Sensors (SCpHSs) by ECD and ORD

In a similar manner as for the SCMs, the chiropical properties of the SCpHSs will be tested in solution and in thin films. Following measurements at different pH will be undertaken in order to test their sensitivity.

d) Corrosion tests

Mixing of the SCpHSs will be performed with paints and tested under corrosion conditions in a similar manner as for the SCMs.

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Máximo 4000 caracteres

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2.- Impacto científico y/o socio-económico del proyecto en caso de tener éxito

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Máximo 2000 caracteres

The costs directly attributable to corrosion in developed countries are 3.1% of the GNP (see the NACE report on the subject available at https://www.nace.org/uploadedFiles/Publications/ccsupp.pdf). Those costs represent a heavy impact on the domestic economies, decreasing the overall competitiveness of the countries where this global problem is not properly adressed.

Most of the corrosion costs have to do with exposure of materials to natural environments (seawater, atmosphere, indoor..), where the protection method usually employed is organic coating. The use of organic coatings in corrosion prevention represent about 80% of the cost attributable to corrosion, thus any improvement in the field will represent an important impact in competitiveness.

Succeeding in the proof of concept of either of the two competitiveness objectives, namely Smart Chiral Monolayers (SCMs) or Smart Chiral pH Sensors (SCpHSs), will open the possibility of a quantitative jump in the world of coating technology, which will push Europe on top of this competitive field. Positive results of the project will boost the industry of organic coatings and will also represent a large change in the paradigma of inspection techniques and methodologies, where the scientific interest of the project lies.

The results from this project will not only greatly benefit the field of corrosion protection, but the use of Smart Chiral Monolayers and pH Sensors will certainly also be applicable for improving coating processes, i.e. car, ship, and aircraft industry among others. As an example, the use of SCMs to reduce the minimum time needed in the coating of an aircraft would reduce important costs.

3.- Personal investigador que participará en el proyecto y descripción del papel de cada uno de ellos
Máximo 2000 caracteres

Xosé Ramón Nóvoa Rodríguez (XRNR): (UVIGO, Spain) Coordinates the corrosion protection studies

Magdalena Cid Fernández (MCF): (UVIGO, Spain) Coordinates the synthesis of the SCFs and SCpHSs

Collaborator – Florian Klappenberger (FK): (TU Munich, Germany) Coordinates the STM studies

José Lorenzo Alonso Gómez (JLAG): (UVIGO, Spain) Coordinates the chiroptical responses studies as well as the different partes of the project togedertogether.

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4.- Autoevaluación de la propuesta
Por favor responda de forma escueta a las siguientes preguntas:

4.1. ¿Cuál o cuáles son, en su opinión, los puntos más importantes por los que su propuesta debería ser seleccionada y financiada?
Máximo 500 caracteres

Certainly the economic impact of this proposal is remarkable. Even when there are risks in the project, the main novelty is the combination of different puzzle pieces, which are already known: coating with organic compounds, self-assembly of chiral compounds and imaging with chiroptical responses. Additionally, the success of the development of SCMs will open a new road for their use in catalysis and sensing.

4.2. ¿Cuál o cuáles son, en su opinión, los puntos más débiles de su propuesta? En otras palabras ¿por qué su solicitud sería rechazada en una convocatoria clásica de otros programas?
Máximo 500 caracteres

There are examples of chiral amplification on surfaces related with the conformation of the molecules, however, not concerning their chiroptical responses. The specific assessment of the chirality of a surface is the main risk of the project and also the main proof of concept to achieve. On the other hand, the imaging of surfaces using chiroptical spectroscopies is known, however, its applicability in industry would need important advances to perfom it at reasonable costs and time.

4.3. Resalte los aspectos de su experiencia investigadora que demuestren que está usted (y, si es el caso, su equipo) preparado para afrontar este estudio.
Máximo 600 caracteres

JLAG and MCF have a large experience on the design, synthesis and characterization of chiral molecules with outstanding chiroptical properties. In collaborations with other research groups, they lead a project funded by the ERC that aims at decyphering the origen of chirality as a function of geometric factors in analogous systems as those proposed herein. FK has vast experience in STM analysis. JLAG in collaboration with FK developed novel Up-standing Chiral Architectures, starting point of this proposal. JLAG has experience on Chiral Amplification via self-assembly processes. XRNR has experi

4.4. Indique si ha presentado esta propuesta, u otra de contenido similar, a alguna convocatoria de proyectos de investigación
Máximo 500 caracteres

This proposal has not been submitted to any other agency. The aim behind this project is to design a broader proposal to be submitted to the ERC in 2014 to the starting grant call.

5.- ¿Cuál es el grado de confidencialidad que solicita para la evaluación de su propuesta?

Muy alto X; **Alto** ; **Normal** ; **No es relevante**

6.- Justificación del presupuesto solicitado para el proyecto EXPLORA
Máximo 2000 caracteres

A postdoc with experience in synthesis and monolayer formation for SCFs and SCMs 60.000 €

This person will perform the synthesis of the SCFs for the SCMs formation. In collaboration with XRNF will perform monolayer for corroson tests and chiroptical properties studies. This person will do short stays at TUM to work closely with FK on the STM studies.

A PhD student for the preparation of SCpHSs and chiroptical studies 40.000€

A PhD student for the preparation of SCpHSs and chiroptical studies.

A solvent purification system for the solvents employed in reactions 50.000 €

This systems will allow for more efficient synthesis as well as improve the safety in the lab.

A HPLC for resolution of compounds 50.000 €

This systems is essential for the purification of the compounds to synthesize.

HPLC columns for resolution of compounds 25.000 €

They are needed for purification with HPLC.

Chemicals for reactions 20.000 €

To perform chemical reactions.

Solvents for reactions and purifications 20.000 €

To perform chemical reactions and purifications

Glassware for synthesis 15.000 €

To perform synthesis and analysis.

Inert gases to perform reactions 1.500 €

to perform reactions

Travels and stays 15.000 €

For conferences as well as short stays at TUM and UVIGO.

Calculations at CESGA 4.000 €

For simulation of chiroptical responses and self-assembly.

CD and ORD accessories 5.000 €

To perform CD and ORD measurements.

ORD adapter for the Jasco-815 35.000 €

To perform ORD measurements.

Preparation of patent 15.000 €

Preparaction and patent presentation.

Publications 10.000 €

Preparation and publication of scientific articles.

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7. Implicaciones éticas y/o de bioseguridad de la investigación propuesta

Si en la aplicación electrónica de solicitud ha contestado **afirmativamente** en alguno de los aspectos relacionados con implicaciones éticas o de bioseguridad allí recogidos, explique los aspectos anteriores referidos a la investigación que se propone, las consideraciones, procedimientos o protocolos a aplicar en cumplimiento de la normativa vigente, así como las instalaciones y las preceptivas autorizaciones de las que dispone para la ejecución del proyecto.
Máximo 3000 caracteres

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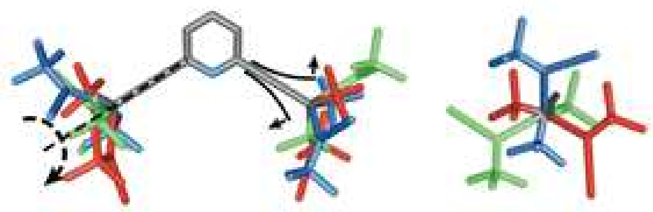
ANEXO I

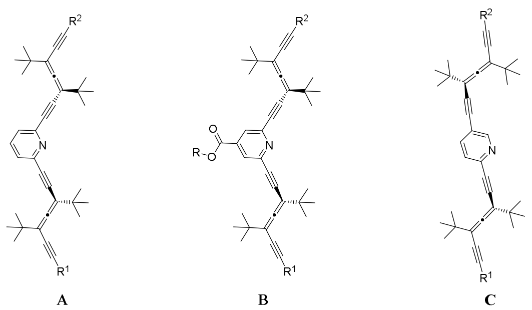
Incluya las fórmulas, tablas, reacciones químicas, etc., que por el tipo de letra del texto del formulario no hayan podido ser insertadas en el mismo. El número de ecuación debe coincidir con su llamada en el texto.

Máximo 1 página

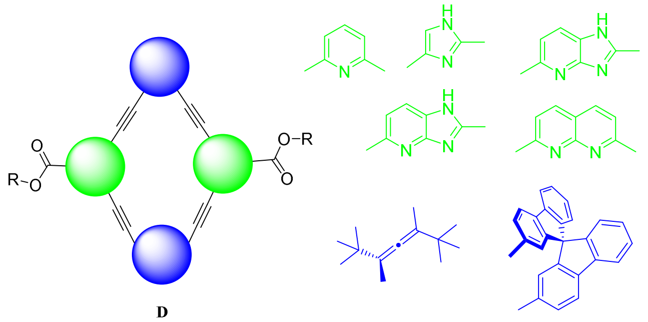
Respete la extensión máxima indicada. Recuerde que en virtud del artículo 11 de la convocatoria **NO SE ACEPTARÁN NI SERÁN SUBSANABLES MEMORIAS CIENTÍFICO-TÉCNICAS** que no se presenten en este formato.



Scheme 1. Visualization of the conformational freedom related to the rotation of the terminal moieties around the alkyne axes (black dashed). Blue, green, and red parts correspond to conformers with different values for θ_1 and θ_2. Further flexibility is introduced by bending of the alkynes (black solid). View along rotation axis for $\theta_1 = 0°$ (blue), 120° (red), and 240° (green). Terminal group shown only for clarity.



Scheme 2. Smart Chiral Framworks (SCF) for Smart Chiral Monolayers (SCMs).



Scheme 3. Smart Chiral pH Sensors (SCpHSs). In green proton receptors and in blue chiral moieties.

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ANEXO II

Únicamente en caso de que se considere necesario para aclarar ciertos aspectos del proyecto, incorpore las imágenes o figuras (formato TIFF, JPEG o GIF) a las que se haya hecho referencia en el texto.

Máximo 2 páginas

Respete la extensión máxima indicada. Recuerde que en virtud del artículo 11 de la convocatoria **NO SE ACEPTARÁN NI SERÁN SUBSANABLES MEMORIAS CIENTÍFICO-TÉCNICAS** que no se presenten en este formato.

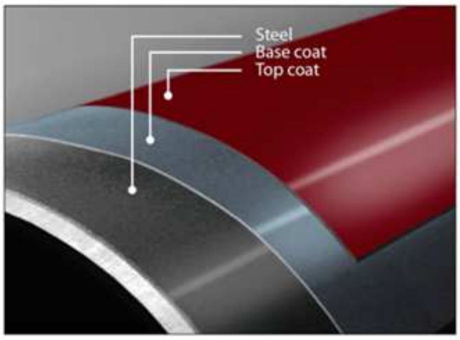

Fig. 1: General structure of a coating system.

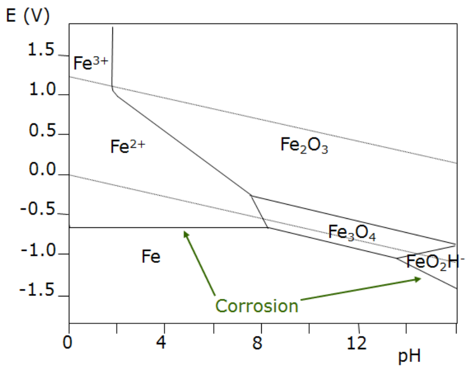

Fig. 2: Stability of iron species *vs* pH.

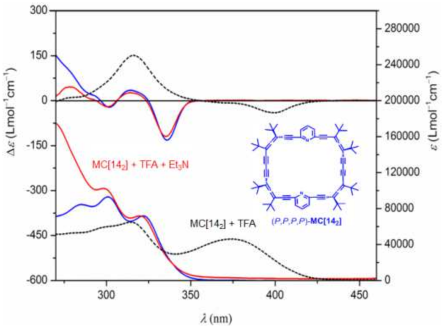

Fig. 3: CD vc pH of pyridine cyclophane. Unpublished results.

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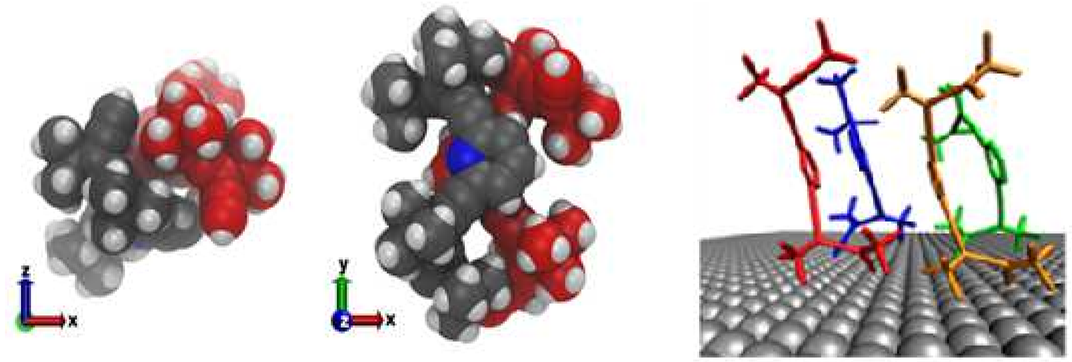

Fig. 4: Up-standing Chiral Architecture (UCA). Top and side view of the dimer conformation as obtained from molecular dynamics simulations using MMFF and illustration of a tetramer. Manuscript in preparation.

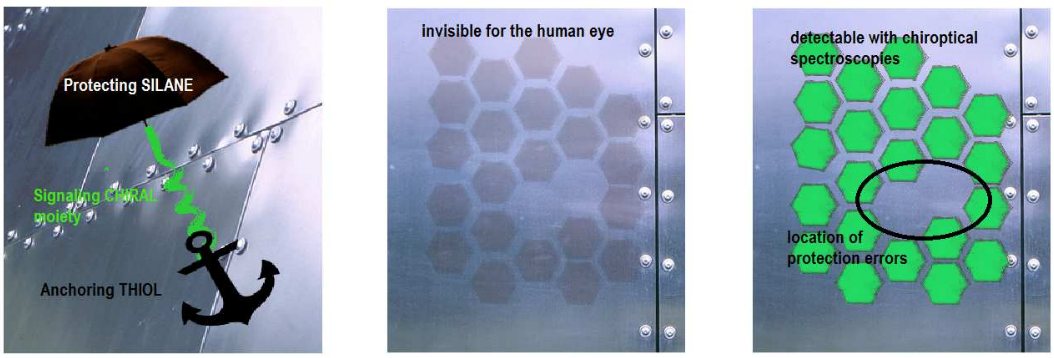

Fig. 5: Smart Chiral Monolayers (SCMs) for Corrosion Protection.

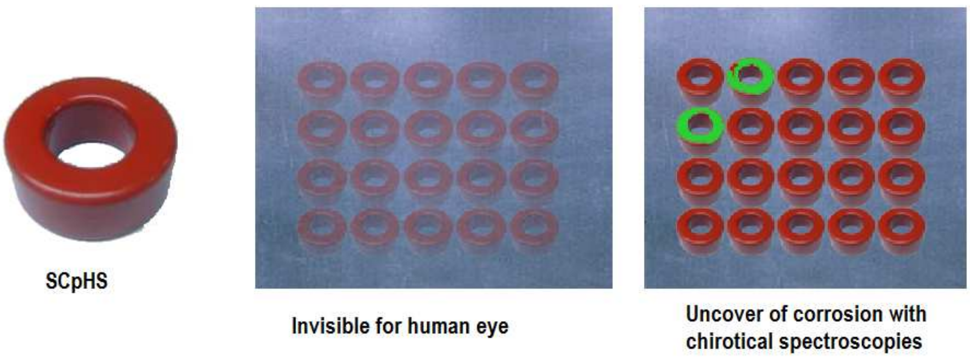

Fig. 6: Smart Chiral pH Sensors (SCpHSs) for Corrosion Mapping.