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Ecocatalysis, a new vision of Green and Sustainable Chemistry

Claude Grison and Yvette Lock Toy Ki

This review is dedicated to ecocatalysis, a concept developed by the Grison group aiming at combining ecology and green chemistry, which could be the vector of sustainable development based on the principle of circular economy. Within this objective, the Grison group has relied on using remediation phytotechnologies, such as phytoextraction, rhizofiltration, and biosorption. These solutions inspired by Nature generate a novel type of biomass, which has become a source of innovation in catalytic chemistry, called ecocatalysis. Ecocatalysts promote key organic syntheses based on sustainable and greener processes.

The biobased approach of ecocatalysts, their vegetal footprint in terms of composition and specific structures allow us to combine the benefits of homogeneous and heterogeneous catalysts, such as selectivity, activity, and recyclability.

Ecocatalysis is setting up the tools of catalytic chemistry for the future, built on the ecological restoration of polluted ecosystems and the respect of Nature.

Addresses

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Keywords

Ecological solutions, Phytotechnologies, Ecological recycling, Ecocatalysis, Sustainable chemistry, Greener processes.

Introduction

In a context of the viral pandemic and ecological crisis, sustainable innovations in chemistry can play a key role in building a different future. In this short review, we propose to share a new vision of green and sustainable chemistry based on a well-established concept named Ecocatalysis [22–24], [9]. Ecocatalysis is at the interface of scientific ecology and sustainable chemistry. Human activities have contributed to climate change,

erosion of biodiversity while led to uncontrolled multiplication of many organisms, reduction of arable lands, destruction of habitat of many species and environmental degradation. It is clear that human behavior must change.

It is interesting to note that our behavior as consumers is changing in agreement with the sustainable development goals of the United Nations. As consumers become more aware, they wonder about the origins of products, the methods used to produce them, the quality of products and the ecological implications of their manufacture and use. Today consumers are increasingly demanding natural and organic products, motivating innovation and the development of Green approaches. Such ethical consumerism is having a major impact on the chemical industry. Safety of ingredients, organic and ethical sourcing of ingredients, ecodesign and eco-friendly processes for Green Chemistry, ecological footprints of processes, waste management, efficiency and Green Economy are all about to become priorities for some chemical companies. The chemical industry is inspired towards positive change.

Green Chemistry and its 12 principles is becoming an interesting and necessary approach [2]. However, Green Chemistry only focuses on the future. There is no answer about the present situation and about what happened in the past.

In this review, we wish to prove that Green and Sustainable Chemistry can take up new challenges solving past, current and preventing future environmental problems. Ecocatalysis, which is the topic of this review, represents such solution. Ecocatalysis relies on using catalysts that are derived from plants, which have been used to restore past and current degraded land and aquatic ecosystems, and that are able to promote key organic syntheses based on sustainable processes.

Restoration of degraded sites as a first step Mining restoration using endemic plant species

The presented strategy is based on the capacity of plants to adapt to stresses caused by high concentrations of metal elements in their environment. New Caledonia is a demonstrative example. This territory is a biodiversity hotspot, home to more than 3000 plant species, 74% of which are endemic. The lagoon is one of the most beautiful on earth and is classified as one of UNESCO's World Heritage sites. This richness is the consequence

of unusual climatic and edaphic conditions, including the presence of high concentrations of Ni and other metallic elements in soil [27].

The endemic biodiversity of New Caledonia includes plants with an impressive ability to tolerate high nickel concentrations in soils. They have the ability to accumulate or hyperaccumulate nickel or manganese from the soil into their aerial parts. For example, the latex produced by the tree *Pycnanandra acuminata* (Sapotaceae) contains 20% Ni [26].

New Caledonian nickel deposits represent 20–25% of the world’s nickel resources. They are thus of primary economic importance, and New Caledonia harbors intensive nickel mining operations. To date, at least 30,000 ha have been affected by mining activities. All New Caledonian mines are open-pit. At the beginning of the exploitation, the vegetation and the topsoil, the uppermost fertile layer of the soil, are removed. Cyclones and other violent storms lead to the leaching of sediment ponds and the erosion of soils. Soils, floodplains, agricultural fields, and rivers are thus contaminated by pollution from open-pit mining. Environments are strongly degraded and their biodiversity is reduced.

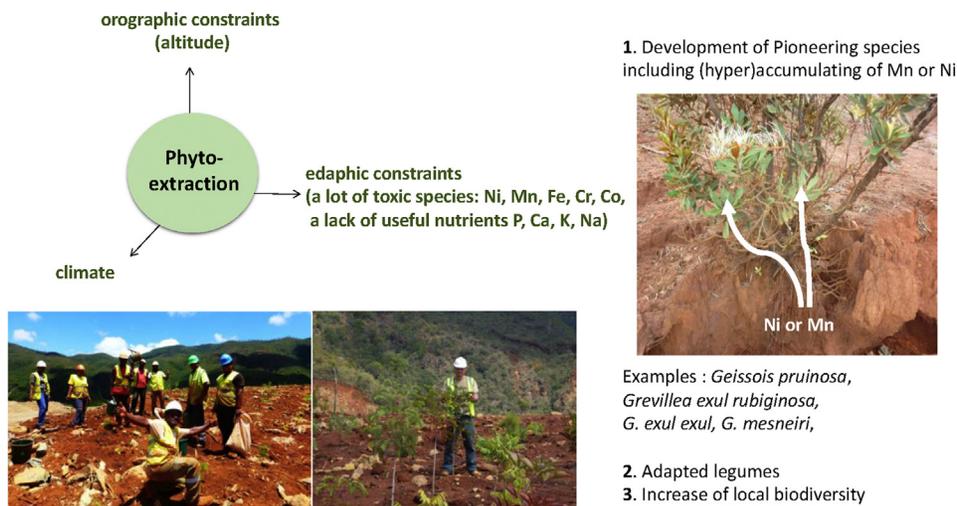
The Grison group has worked for a decade in New Caledonia to develop a vast program of ecological rehabilitation of such mining sites, with the logistical support of French mining operators (K.N.S. and S.L.N.) and of Agronomic Institute of New Caledonia [22–24,28,29]. This program is based on only using endemic species, especially plants that are

hyperaccumulators of nickel and manganese. Restrained by altitude, by tropical climate and mainly by edaphic conditions, with many toxic elements and a scarcity of nutrient elements, the ecological rehabilitation of these sites followed a three-step plan (Figure 1). First pioneer Ni- and Mn-hyperaccumulating plants were used. Then pioneer nitrogen-fixing leguminous species adapted to these conditions were introduced, in order to increase nutrient in soil and to finally introduce plants with more demanding ecological requirements and restore much of the local biodiversity.

Restoration of aquatic ecosystems

There is a clear link between pollution of soils and pollution of aquatic ecosystems, as water easily diffuses metallic elements in the environment. Therefore, the conservation of the water resource is an integral part of our research on ecological rehabilitation. The Grison group has conducted several experiments to remove metal pollution from aquatic ecosystems using two phytotechnologies: rhizofiltration [18] [5–7] and biosorption [25,30,20]. Rhizofiltration was based on using specific aquatic plants that have an exceptional capacity to concentrate metallic pollutants in roots. Roots of aquatic plants exhibit an ideal chemical structure naturally rich in carboxylate groups, which are complex metallic elements. These performances being due to a passive and not an active accumulation, the group has developed a method to use powdered roots instead of the living plants to biosorb metallic pollutants [25,30]. The root powder was used as a plant filter, in batch mode or in a continuous process, to clean wastewater from chemical industrial operations and quarrying,

Figure 1



mining, and agricultural activities (Figure 2). Interestingly biosorption presented similar efficiency to rhizofiltration, with the advantage of using a non-living, storable, and available biomaterial.

This flexible and robust tool can be applied in different contexts: capture of strategic metals such as Pd and Rh, whose prices are exploding, of primary metals such as Zn, Mn, Ni, Cu, and Co, of which the global depletion is worrying, and of toxic metals such as As, Pb, and Cd [25].

However, the development of this ecotechnology is still restricted by the fact that contaminated biomass is not recovered; the aerial parts of hyperaccumulating plants and metal-biosorbed plant powder have been considered as contaminated waste. The Grison group has developed a strategy to overcome this economic restriction of ecological rehabilitation.

Methods allowing an unprecedented recovery of metallic elements accumulated or biosorbed by biomass, are developed. Leaves, roots and plant powder enriched in metallic elements are transformed into metal catalysts, called ecocatalysts, for use in applications of organic chemistry.

Ecocatalysis as valorization of contaminated biomass (leaves, roots, powders)

Preparation and composition of ecocatalysts

A simple and easy process for producing ecocatalysts has been designed. The biomass, no matter its origin –

leaves, roots or powders – was subjected to a thermal treatment under air, in order to remove organic matter while retaining the metal salts. According to the plant species and the treatment, three types of ecocatalysts could be prepared: Lewis and/or Brønsted acid ecocatalysts called Eco-MCl, reducing ecocatalysts called Eco-M(0) and oxidative ecocatalysts called Eco-M_{ox} (Table 1).

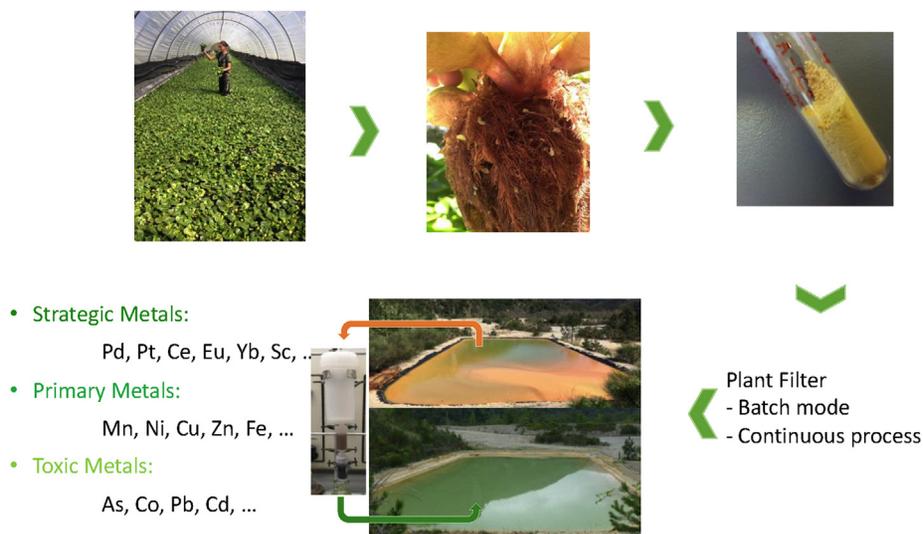
Eco-MCl were prepared from the thermal residues treated by hydrogen chloride forming new anions, such as chlorides [11]. Eco-M(0) were prepared from the thermal residues treated by formic acid generating formate salts, followed by a controlled thermal decomposition, leading to the Eco-M(0) at an oxidation state of zero (Escande et al., 2017a). And Eco-M_{ox} were composed of the thermal residues and directly used without any chemical activation [3].

Ecocatalysts are original polymetallic systems, which combine a mixture of the phytoaccumulated transition metal and physiological components such as Mg, Ca, Fe, Na, and K. The metallic chemodiversity of ecocatalysts leads to unusual metal/substrate interactions in solution. The structure and morphology of the ecocatalysts were characterized in detail.

Structure of ecocatalysts

It is noteworthy that the structure of ecocatalysts mainly depends on the plant species from which they derive and the chemical and/or thermal treatment necessary for their preparation.

Figure 2



Ecological treatment of industrial effluents by biosorption based on plant filters.

Eco-MCl, all derived from hyperaccumulators, exhibited similar structures. Two main bimetallic species were observed: a double salt of Ca and Mg, CaMg_2Cl_6 , called tachyhydrite and a mixed salt of potassium and the transition metal that was hyperaccumulated (Zn, Ni, Mn, Pd), forming K_2ZnCl_4 [12], KNiCl_3 [21], KMnCl_3 , $\text{K}_3\text{NaMnCl}_6$ [19], K_2PdCl_4 (Clave et al., 2017) and K_2PdCl_6 [1]. Eco-MCl derived from accumulators presented a mixed salt of potassium and magnesium, KMgCl_3 [8], whereas Eco-MCl derived from nonaccumulators showed a mixture of potassium–magnesium and calcium–magnesium salts, KMgCl_3 and CaMg_2Cl_6 [10] (Table 1).

Eco-M(0) derived from hyperaccumulators presented other characteristic structures: Ni(0), along with an unexpected alloy, FeNi_3 [17].

Eco-M_{ox} derived from hyperaccumulators presented a natural richness in two unusual and valuable mixed calcium–manganese oxides, $\text{Ca}_2\text{Mn}_3\text{O}_8$ and CaMnO_3 , which exhibit crystalline structures close to that of CaMn_4O_5 , the natural cofactor of Photosystem II [3].

In general, Inductively Coupled Plasma Mass Spectrometry (ICP-MS), X-ray powder diffraction (XRD), X-ray absorption near edge structure (XANES), and

Table 1

Structure of ecocatalysts.				
Species	Phytotechnology	Hyper(phyto) accumulators Good accumulators	Poor accumulators	Nonaccumulators
Ecocatalysts: Eco-MCl:				
Lewis acids/coupling agents – HCl activation				
<i>Noccaea caerulescens</i>	Phytoextraction of Zn	K_2ZnCl_4	/	/
<i>Anthyllis vulneraria</i>		CaMg_2Cl_6		
<i>Arabidopsis halleri</i>		K_2ZnCl_4		
<i>Geissois pruinosa</i>	Phytoextraction of Ni	KNiCl_3		
		CaMg_2Cl_6		
<i>Anisopappus chinensis</i>	Phytoextraction of Cu	Amorphous structure		
<i>Grevillea exull</i>	Phytoextraction of Mn	KMnCl_3		
<i>Grevillea exul rubiginosa</i>		$\text{K}_3\text{NaMnCl}_6$		
<i>Grevillea mesneiri</i>		CaMg_2Cl_6		
<i>Grevillea gillivray</i>				
<i>Lolium multiflorum</i>	Rhizofiltration of Cu	Amorphous structure		
<i>Bacopa monnieri</i>				
<i>Eichhornia crassipes</i>	Rhizofiltration of Pd	K_2PdCl_4		
<i>Eichhornia crassipes</i>				
<i>Lolium multiflorum</i>				
<i>Eichhornia crassipes</i>	Biosorption of Pd	K_2PdCl_6		
<i>Ludwigia peploides</i>				
<i>Salix schwerinii</i> <i>Salix viminalis</i>	Phytoextraction of Zn	/	KMgCl_3	
<i>Grevillea rosa ssp. jensinkii</i>	/			
<i>Salix alba</i>			/	CaMg_2Cl_6
<i>Betula</i>				KMgCl_3
<i>Fagus</i>				
<i>Acer</i>				
<i>Platanus</i>				
Ecocatalysts:				
Eco-M(0):				
Reducing agents - HCOOH activation				
<i>Psychotria gabriellae</i>	Phytoextraction of Ni	Ni FeNi_3	/	/
Ecocatalysts:				
Eco-M_{ox}:				
Oxidizing agents – No activation				
<i>Grevillea exul</i>	Phytoextraction of Mn	$\text{Ca}_2\text{Mn}_3\text{O}_8$	/	/
<i>Grevillea exul rubiginosa</i>		CaMnO_3		
<i>Grevillea mesneiri</i>				
<i>Grevillea gillivray</i>				

Extended X-Ray Absorption Fine Structure (EXAFS) analyses clearly show that Eco-MCl, EcoM(0) and EcoM_{ox} are not a juxtaposition of simple metal chlorides, their composition is much more complex. It seems that Eco-M have a vegetal foot-print in terms of their composition and their crystallization pathways [19]; which are interesting to consider for studying their catalytic activity.

Theoretical calculations

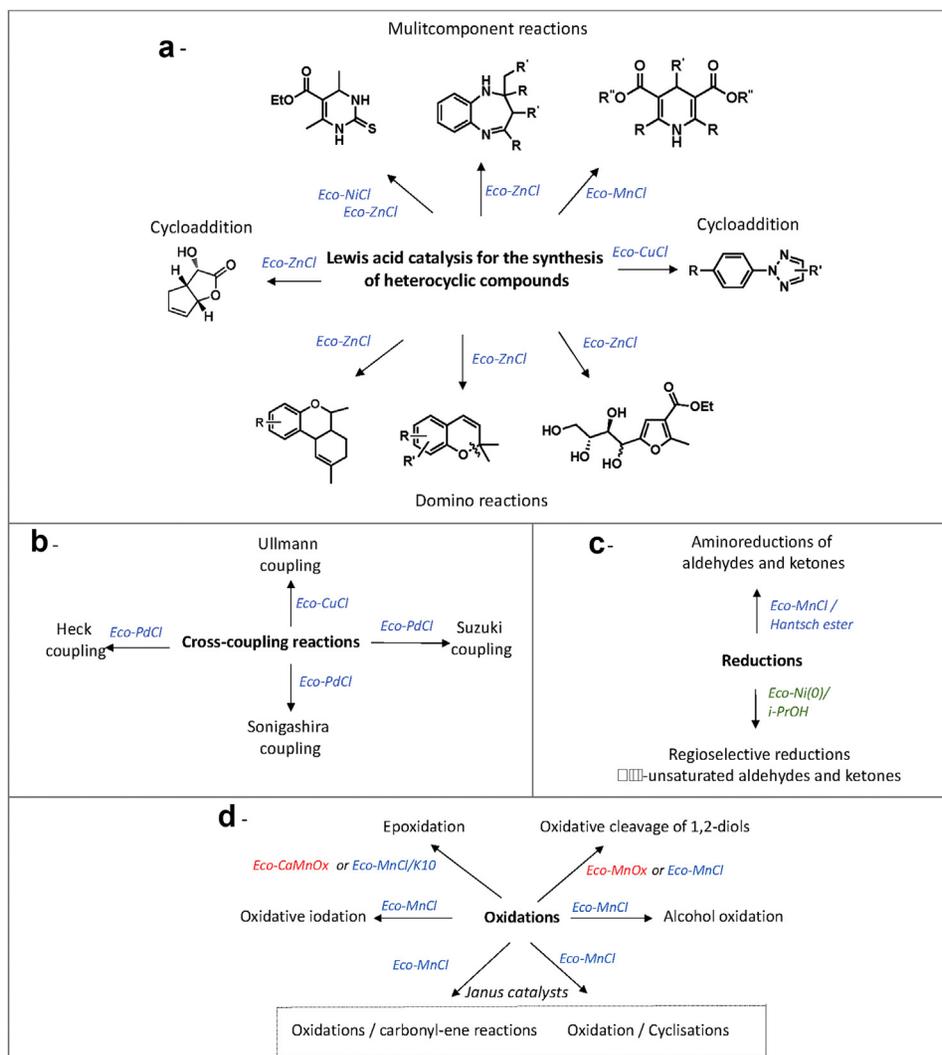
Density Functional Theory (DFT) calculations were carried out on several ecocatalysts to further characterize a link between structure and catalysis activity. DFT calculations in parallel of infrared study of pyridine adsorption/desorption have shown that Eco-MCl

catalysts follow the Gutman theory, that is to say the 'pileup' and 'spillover' effects: the charge densities of the Lewis acid and base are redistributed. The partial charge of transition metals is increased by interaction with supplementary chlorides as for example KMgCl₃ and CaMg₂Cl₆ compared with MgCl₂ and CaCl₂ [10]. As a consequence, the softness of the mixed salts is different, and their Lewis acid properties are superior than that of conventional metal chlorides [10,19], which is worth considering for their reactivity in organic synthesis.

Reactivity of ecocatalysts in organic synthesis

Ecocatalysts can be used as heterogeneous and homogeneous catalysts in synthetic transformations, allowing

Figure 3



Reactivity of ecocatalysts in organic synthesis. (a): Lewis acid ecocatalysis, (b) Cross-Coupling reactions, (c) Reductions, (d) Oxidations).

access to molecules with high added value for fine and industrial chemistry. The activity, selectivity, and recyclability of ecocatalysts have been illustrated in numerous reactions, such as Lewis and/or Brønsted acid-catalyzed reactions, coupling reactions, reductions, and oxidations.

Lewis or brønsted acid catalysis

The Lewis and/or Brønsted acid character of ecocatalysts was demonstrated by studying their reactivity towards the cyclic ketal derived from bromopropiophenone. The reaction can lead to a mixture of components depending on the acidic properties of the catalyst (Brønsted acid, hard Lewis acid, and soft Lewis acid). According to the nature (Lewis/Brønsted acid) ecocatalyst, multicomponent, cascade reactions, or cycloadditions lead to the direct preparation of complex heterocycles such as thiopyrimidinones [21], 1-*H*-1,5-benzodiazepines, dihydropyrimidines, cannabinoids, 2-*H*-chromenes [14], 1,2,3-substituted triazoles [6], lactones [13], and capped RNA [31] (Figure 3). Among those, the asymmetric synthesis of furoate compounds with a chiral group should be emphasized [12].

Cross-coupling reactions

Eco-MCl have also been used in a wide range of cross-coupling reactions such as palladium, copper-catalyzed C-, N-, and O-arylation reactions (Figure 3). Among the numerous Eco-MCl, Eco-Pd catalysts lead to the best results. They present an exceptional reactivity in Suzuki, Heck, and Sonogashira coupling reactions even with a low loading in Pd (0.0025–0.1 mol%). Such reactivity might be explained by the morphology of Eco-Pd catalysts, which are composed of small and stable nanoparticles of Pd that are nonaggregated and perfectly dispersed on the plant-derived mineral matrix [18]. Moreover, Eco-Pd-catalyzed cross-coupling reactions have been optimized to become technically and economically practicable. Green solvents (glycerol, butanol, water) in moderate reaction time and temperature were used without any ligand, cocatalyst, or additive, allowing an easy recycling and reusing of Eco-Pd [7,1].

The use of Eco-MCl in cross-coupling reactions could provide an effective solution for the depletion of platinum, along with significant environmental benefit.

Ecocatalyzed reductions

Two types of reductions have been investigated by ecocatalysis, reductive aminations and reductions of carbonyl compounds (Figure 3).

The reductive amination of carbonyl compounds is catalyzed by Eco-MnCl, which constitutes the first example of reduction with a Mn promoter. The reaction is conducted in solvent-free conditions, with the easily

prepared and safe Hantzsch ester as reducing reagent. This methodology was applied to the reductive amination of various ketones, including two precursors of pharmaceutically active compounds [15].

The reductions of carbonyl compounds is catalyzed by Eco-Ni(0) allowing hydrogenation with isopropanol as an eco-friendly reagent and solvent. The regioselectivity of reduction of the carbonyl group for the α,β -unsaturated carbonyl compounds should be noted. This performance can be explained by the particular structure of Eco-Ni(0) composed of an unusual species, FeNi₃. Moreover, its morphology is closed to that of montmorillonite K10 in terms of specific area and pore size [17].

These catalytic systems constitute a valuable alternative for reductions to classical catalysts based on precious metals.

Ecocatalyzed oxidations

A wide range of ecocatalyst rich in Mn have been described for oxidative transformations (Figure 3). For example, Eco-MnCl and Eco-MnO_x lead to a practical and elegant solution to the long-standing challenge of oxidative cleavage of 1,2-diols into aldehydes or ketones [4]. Supported Eco-MnCl_x and Eco-CaMnO_x show great potential as green catalysts for economically valuable reactions such as epoxidation, alcohol oxidation or oxidative iodation [4]. Interestingly, the original composition of Eco-CaMnO_x catalysts, closed to the natural cofactor CaMn₄O₅ of Photosystem II, led to distinctive catalytic behaviors compared to previously studied Eco-MnCl, allowing the preparation of sensitive epoxides [3]. Finally, Eco-MnCl has been shown to act as 'Janus catalysts' by promoting tandem sequences of multicomponent type oxidations, cyclizations and carbonyl-ene reactions [16].

Conclusion

Ecocatalysis has emerged as a new Green and Sustainable Chemistry approach with a high potential for the valorization of metal-rich biomass. The metal-rich biomass obtained from phytoextraction, rhizofiltration, and biosorption can be directly used as catalysts in organic chemical reactions. Ecocatalysis provides the first perspective of enhancing the value of unique metal-rich biomass from remediation ecotechnologies and promoting a new field in Sustainable Chemistry. The results show that polymetallic ecocatalysts could perform better and provide much higher selectivity than classical homogeneous and heterogeneous catalysts.

The development of this new concept is creating a paradigm shift in sustainable and green chemistry: metallic wastes are becoming new, ecofriendly and efficient catalytic systems.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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- * of special interest
- ** of outstanding interest

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