Photochemistry of a Chiral Salen Aluminum Complex in Nonconventional Solvents: Use of Imidazolium Ionic Liquids and Chiral Alcohols

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Received: March 18, 2007; In Final Form: May 10, 2007

The photochemistry of a chiral (salen)aluminum(III) chloride complex has been studied in nonconventional solvents, namely, two imidazolium ionic liquids differing on the hydrophobicity (hydrophilic BF_4^- or hydrophobic PF_6^- counter anions) and in chiral 2-butanols (*R* and *S*). Upon 355 nm laser excitation, the same transient absorption spectrum (with some solvatochromic shift in λ_{max}) was recorded in all cases and assigned to the (salen)Al(II) complex with radicaloid character at the metal atom. This intermediate arises from the photoinduced homolytic cleavage of the apical Al−Cl bond. The half-life of this radicaloid Al(II) species varies depending on the solvent, indicating that its reactivity is governed by the nature of the ionic liquid and also on the *R or S* configuration of the chiral alcohol.

Introduction

Chiral metal salen complexes are among the most powerful enantioselective catalysts.[1−5] The nature of the Schiff base metal is crucial regarding the catalytic activity of the complex to promote different enantioselective reactions. In particular, aluminum salen complex is an exceedingly active enantioselective catalyst for asymmetric aldol condensations, the Strecker reaction (the enantioselective addition of hydrogen cyanide to an aromatic imine), and for the CO_2 insertion into epoxides among other reactions.[6−16]

Motivated by the interest of these metallic complexes in catalysis, some recent studies have focused on the photochemistry of chiral metal salen complexes in an attempt to provide complementary information about their properties and behavior that can be useful to understand and rationalize their performance under different conditions.[17−24] For instance, the salen oxomanganate(V), which is a relevant intermediate in conventional catalytic epoxidation of alkenes, can be generated photochemically and its reactivity and lifetime studied by transient spectroscopy.[25] Analogously, a correlation between the lifetimes of the photogenerated charge separated excited state and the epoxidation activity of nickel salen complexes has also been reported.[26]

Besides their enormous interest in enantioselective catalysis, salen metal complexes have been found to exhibit interesting properties due to their photo- and electroluminescence properties.[22,23,27−31] In particular, the remarkable emission properties of aluminum complexes such as aluminum hydroxyquinoline (Alq3) has been widely exploited in the development of electroluminescent devices.[28,30,32−34]

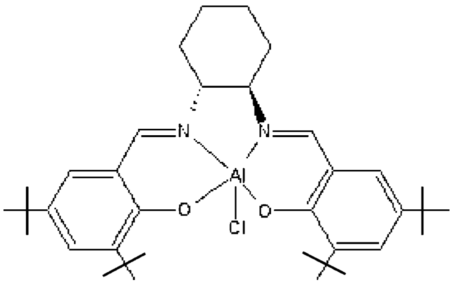
The photoluminescence and photochemistry of chiral pentacoordinated aluminum salen complexes in acetonitrile has been previously reported.[19] In addition to exhibiting a strong photoluminescence, the photochemistry of (salen)aluminum(III) chloride has been interpreted by assuming the formation of an Al(II) radicaloid intermediate arising from the homolytic cleavage of the apical Al−Cl bond.[19] Considering the influence of solvents in catalysis and particularly the suitability of ionic liquids as solvents for metal salen complexes,[35−38] herein we have proceeded to study the photochemistry of a chiral aluminum salen complex in two representative imidazolium ionic liquids. Analogously, we have studied the photochemical properties of the chiral aluminum salen in enantiomerically pure (*R*)- and (*S*)-2-butanols. Enantiomerically pure solvents can interact stereoselectively with the ground and/or excited states of chiral molecules, introducing some degree of asymmetric induction on photochemical processes.[39−43] This information can be of interest to understand the catalytic activity.

The influence of the solvent on the outcome of photochemical reactions is well documented.[44,45] Factors as polarity, viscosity, and hydrogen-bond donor or acceptor capacity can affect profoundly the photochemical behavior of dissolved molecules. The use of ionic liquids to carry out photochemical reactions is a topic of current interest.[46−51] In the present study, we want to establish the influence of the media on the photochemistry of a catalytically relevant complex like chiral salen Al(III). This type of work can serve to establish relationships between the photophysics and the catalysis. Al(III) salen is a pentacoordinated metal complex exhibiting a square pyramidal structure, with the salen ligand occupying a pseudoequatorial position and the chloride atom in apical ligand (Scheme 1).

The photophysics and photochemistry of Al(III) salen have been determined by means of fluorescence measurements and laser flash photolysis experiments.[19] The first part of this work presents the photochemistry of chiral aluminum salen complex in 1-butyl-3-methylimidazolium-hexafluorophosphate (bmim-PF_6) and 1-butyl-3-methylimidazolium-tetrafluoroborate (bmim-BF_4) ionic liquids. These molten salts are ionic organic compounds whose physical state is liquid at room temperature.[52−55] They have the advantage of their nonvolatile nature, lack of toxicity for the atmosphere, and a high solubility ability for a wide range of organic compounds. Ionic liquids have recently attracted considerable interest as green solvents to perform catalytic reactions.[54,55] In particular, ionic liquids have been found to be especially suited to perform catalytic reactions using chiral salen metal complexes, whereby extremely high enantiomeric excess values have been obtained in some cases.[1,36] Given the general applicability of chiral salen aluminum

10.1021/jp0721604 CCC: $37.00

SCHEME 1: (Salen)Al(III)−Cl



complex as enantioselective catalysts, the second part of this report deals about the degree of asymmetric discrimination in the photophysics of chiral aluminum salen as a function of the configuration of enantiomerically pure (*R*)- and (*S*)-2-butanol.

Experimental

The bmim-PF_6 and bmim-BF_4 ionic liquids employed in this work were commercial samples supplied by Solvent Innovation. Imidazolium ionic liquids were dried by heating at 50 °C under 30 Torr for at least 60 min before using them. The chiral (*R*)- and (*S*)-2-butanols and the chiral aluminum salen complex (*R*,*R*)-*N*,*N′*-bis(3,5-dibutylsalicylidene)-1,2,-cyclohexanediaminoaluminum(III) chloride were supplied by Aldrich and used as received. To prepare the solution of the aluminum salen solid in ionic liquids, the complex was first dissolved in the minimum amount of acetonitrile (20 $mg{\cdot}mL^{-1}$), and then an appropriate volume of this solution was added to bmim-PF_6 or bmim-BF_4, stirring magnetically the homogeneous mixture for at least 15 min. Acetonitrile was then thoroughly evacuated from the ionic liquids under vacuum. The salen aluminum was directly dissolved in the chiral (*R*)- and (*S*)-2-butanols.

Before the photochemical measurements, the samples were purged with nitrogen or oxygen for at least 15 min. All the measurements were carried out in Suprasil quartz cuvettes capped with septa. UV−Visible spectra were recorded in solution with a Shimadzu PC spectrophotometer, using the corresponding solvents as reference. The emission and excitation spectra were recorded in an Edinburg FS900 spectrofluorimeter provided with a Czerny−Turner monochromator. Emission and excitation slits were maintained unchanged during the experiments. Laser flash photolyses were carried out in a LuzChem nanosecond laser system using the third harmonic of a Surelite Nd:YAG laser (355 nm, 7 ns fwhm, 18 $mJ{\cdot}pulse^{-1}$) for excitation. The data were captured with a Tecktronic TDS 640 A oscilloscope and were transferred to the PC that provided data storage capability and at the same time controlled the data acquisition.

Results and Discussion

Photochemistry of Salen Aluminum(III) Chloride in bmim-PF_6 and bmim-BF_4 Ionic Liquids. As commented before, there have been several reports describing the use of ionic liquids as solvents to develop a homogeneous and reusable system to perform enantioselective reactions catalyzed by chiral metal salen complexes.[1] In these studies, it was found that the counteranion accompanying the imidazolium cation plays a remarkable role on the enantiomeric excess of the resulting product.[14,36,38,56] As a general rule, PF_6^- leads to much better e.e. values than BF_4^-. It was suggested that the relative changes in the hydrophilicity/hydrophobicity balance as consequence of the increase in the fluorine content (BF_4^- is known to be more hydrophilic than PF_6^-) is the factor responsible for this remarkable influence of the anion on the catalysis.

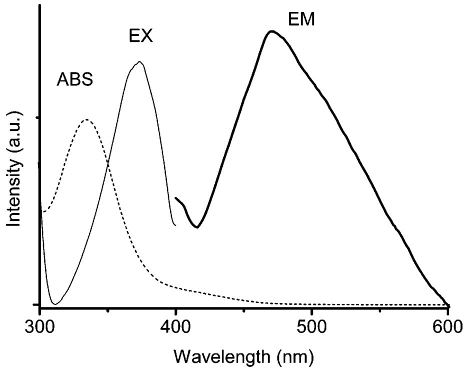


Figure 1. Emission (EM, $\lambda_{exc} = 370$ nm), excitation (EX, $\lambda_{em} = 470$ nm), and absorption (ABS) spectra of salen aluminum complex (1.3×10^{-4} M) in bmim-BF_4 purged under N_2.

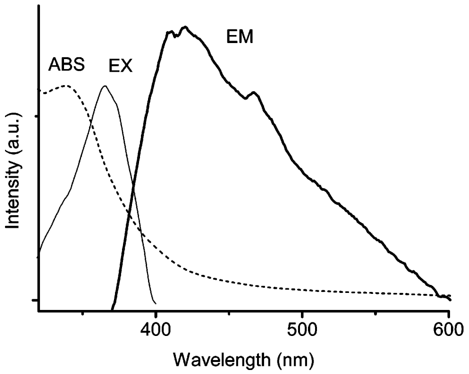


Figure 2. Emission (EM, $\lambda_{exc} = 370$ nm), excitation (EX, $\lambda_{em} = 418$ nm), and absorption (ABS) spectra of salen aluminum complex (1.3×10^{-4} M) in bmim-PF_6 purged under N_2.

To provide additional information on the influence of the counteranion of metal salen complexes, we proceeded to characterize the photophysics of the aluminum salen complex in the bmim-PF_6 and bmim-BF_4 ionic liquids. We were particularly interested in determining the variations of the photophysics due to the nature of counteranion compared with the results reported in acetonitrile.[19]

Ionic liquids are transparent at wavelengths longer than 320 nm, thus making it possible to record the optical spectrum of aluminum salen beyond this wavelength. The UV−visible absorption spectra of salen Al(III) in bmim-BF_4 or bmim-PF_6 ionic liquids exhibit a LMCT band at 335 nm, in good agreement with the λ_{max} of the same complex in acetonitrile (335 nm). Notably, in imidazolium ionic liquids, the emission spectra recorded upon excitation at 370 nm show maximum intensity at very different wavelengths. Thus, λ_{em} for bmim-BF_4 (Figure 1) and bmim-PF_6 (Figure 2) were measured at 471 and 418 nm, respectively.

These λ_{em} shifts depending on the hydrophobic/hydrophilic nature of the ionic liquid were also observed on the excitation spectra recorded by monitoring at the maximum emission wavelength. It is well-known that the polarity of the solvent influences the spectral maxima of the dissolved molecules.[57] The dipolar forces of the ionic liquids varied with the nature of their anion. It is proposed that the higher polarity of bmim-BF_4 as compared to bmim-PF_6 causes the remarkable shifts observed on the luminescence spectra.[58]

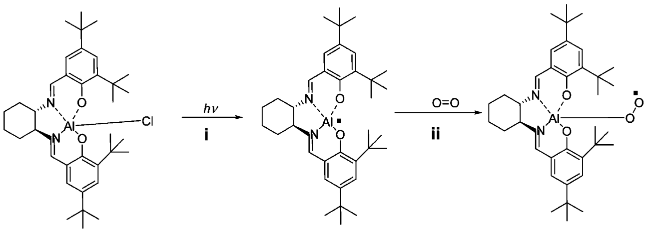
The singlet excited-state lifetime was estimated by fitting the temporal signal decay of the emission recorded in the ionic liquid to two consecutive first-order kinetics. The values

TABLE 1: Photochemical Parameters Measured for the Al(III) Salen in Different Solvents (Estimated Errors of the Quantum Yield and Lifetime Measurements are below ± 0.02 and ± 0.3, Respectively)

solvent	ϕ_{fl}	τ_s (ns)	τ_r (μs)
MeCN	0.35	4.8	7
bmim-BF_4	0.07	**τ_1= 9.4 (11%)** **τ_2=16.0 (89%)**	138
bmim-PF_6	0.07	**τ_1= 5.2 (92%)** **τ_2=13.6 (8%)**	>400
(*R*)-2-butanol	0.95	12.8	4.4
(*S*)-2-butanol	0.84	12.8	18.6

obtained for salen Al(III) in the ionic liquids bmim-PF_6 and bmim-BF_4 are grouped in Table 1. No effect of the O_2 purging has been observed on the luminescence spectra. In contrast to acetonitrile, for which a single monoexponential decay is observed, the decay of (salen)Al(III)−Cl in ionic liquids becomes more complex and much longer lived. The fitting to a suite of two exponential decays may be interpreted as indicating the existence of two different complex populations, one of them similar to that found in acetonitrile and a second one in which a strong association between the metal site and the anion present in the ionic liquid is taken place. The absolute photoluminescence quantum yields in ionic liquids were determined by comparison with the quantum yield of an optically matched solution of salen Al(III) complex in acetonitrile (ϕ_{fl} = 0.35), the resulting Φ values being significantly lower (Table 1).

Aluminum complexes are very often strongly photoluminescent compounds in conventional solvents or in the solid state. The dramatic decrease in the emission quantum yield may indicate that the aluminum complex is strongly interacting with the nucleophilic anionic part of the ionic liquids through coordination of the positive aluminum atom with the fluoride of the BF_4^- or PF_6^- anions.



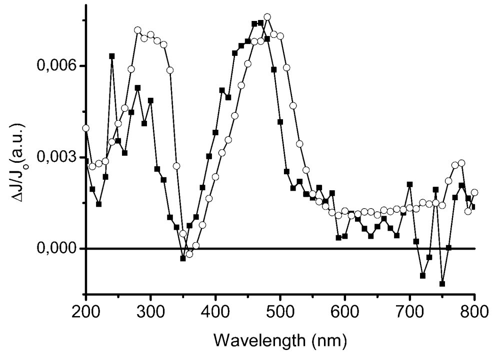


Figure 3. Transient absorption spectra of N_2-purged solution of salen aluminum complex (1.3 × 10^{-4} M) in bmim-BF_4 (■) and bmim-PF_6 (○) recorded 35 μs after 355 nm laser pulse.

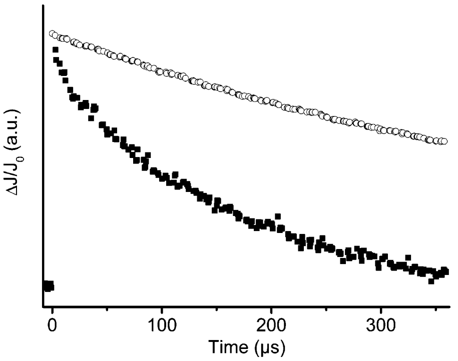


Figure 4. Decays of the N_2-purged salen Al(II) radical in bmim-BF_4 (■) and bmim-PF_6 (○) monitored at 470 and 480 nm, respectively.

Ionic liquids are not transparent media at 266 or 308 nm, giving rise to the generation of short-lived transients upon laser excitation at these two wavelengths. In contrast, bmim-BF_4 and bmim-PF_6 ionic liquids do not give any response using 355 nm excitation, making thus possible the study of the photochemistry of salen Al(III) at this wavelength. The transient absorption spectra of salen Al(III) complex in bmim-BF_4 and bmim-PF_6 purged under N_2 recorded 35 μs after 355 nm excitation are shown Figure 3. Assignment of the transient species was based on the excellent agreement of the spectral features of the transient with absorption maxima at around 300 and 480 nm and bleaching of the ground state at 350 nm with the transient absorption spectra recorded in acetonitrile that corresponds to the salen Al(II) radical generated upon homolytic bond breaking of the Al−Cl bond (step i in eq 1).[19] The temporal profile is very sensitive to the nature of the solvent, being that the aluminum centered radical is considerably much longer lived in imidazolium ionic liquids (hundreds of μs) than in acetonitrile ($\sim$7 μs). We notice, however, that this transient is shorter-lived in bmim-BF_4 than in bmim-PF_6 (Figure 4). Table 1 also lists the half-life of the Al(II) radicaloid species in ionic liquids calculated from the best fit of the signal decay to a monoexponential kinetics. In agreement with the assignment of the transient to a radicaloid species, oxygen strongly quenches the transient spectrum (step ii in eq 1). O_2 is poorly soluble in ionic liquids, but the long lifetime of this Al(II) species, living hundreds of μs, still makes possible the quenching in spite of its low concentration and slow molecular diffusion of the oxygen in the ionic liquids.[59] With the long lifetime of the Al salen radical in imidazolium ionic liquid, it is worth commenting that this indicates that this transient species is not able to react with any H atom donor present in the media. Thus, while water is a common impurity present in the ionic liquid, this molecule is extremely poor H atom donor. On the other hand, it has been reported[59] that ketone excited states are able to abstract a H atom from the 2-position of the imidazolium ring. This process is obviuosly not observed in our case. Most probably, the lower bond energy of Al−H compared to C−H makes this process thermodinamically uphill in our case.

Photochemistry of Chiral Salen Al(III) in Enantiomerically Pure (*R*)- and (*S*)-2-butanols. The UV−visible spectra of the aluminum complex in (*R*)- and (*S*)-2-butanol has absorption bands at 232 and 280 nm assigned to the ligand-centered transitions and a weaker band at 358 nm due to the LMCT. Salen Al(III) in nitrogen-purged 2-butanols exhibits an intense fluorescence band (λ_{em} = 470 nm) upon excitation at 350 nm. The relative quantum yields of fluorescence were 0.95 and 0.84 in (*R*)- and (*S*)-2-butanol, respectively, by comparison with the quantum yield obtained in acetonitrile (Φ 0.35). This high-fluoresecence quantum yield indicates that the homolytic Al−Cl bond breaking observed in acetonitrile is considerably disfavored in butanols. Probably, H bridges between the solvent and the Al metal ion are responsable for this deactivation of the excited state. The excitation spectrum coincides remarkably well with the absorption spectrum and shows a peak at 358

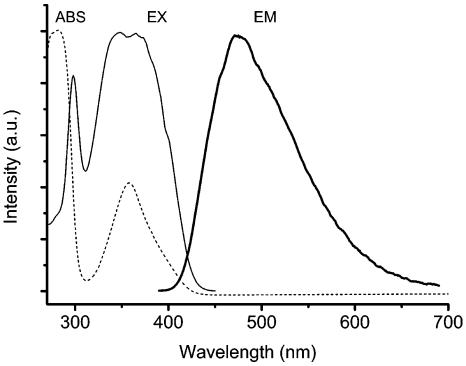
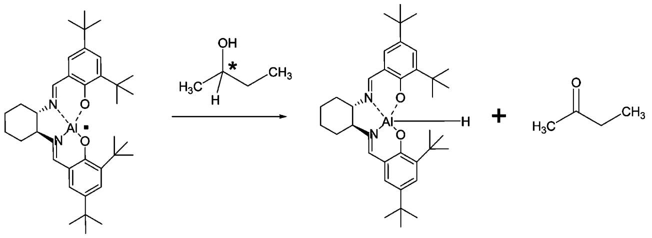


Figure 5. Emission (EM, $\lambda_{exc} = 370$ nm), excitation (EX, $\lambda_{em} = 470$ nm), and absorption (ABS) spectra of salen aluminum complex (1.3×10^{-4} M) in N_2-purged (*R*)-2-butanol.

nm, providing convincing evidence of the LMCT transition as responsible for the photoluminescence (Figure 5). Fitting the emission temporal decay, single-exponential kinetics allowed us to estimate the singlet lifetime in (*R*)-2-butanol as $\tau = 12.8$ ns. This value is close to the singlet lifetime measured in ionic liquids. However, the single-exponential kinetics observed in (*R*)-2-butanols is expected for a homogeneous medium containing only one emitting species. O_2 purging produced the quenching of the luminescence signal ($\tau = 6$ ns). The decay of the singlet excited state after N_2 purging was rigorously identical by using (*S*)-2-butanol as solvent, and the quenching of the singlet excited state by oxygen was indistinguishable in both chiral (*R*) and (*S*) solvents.

The laser flash photolysis of the salen Al(III) in enantiomerically pure 2-butanols was carried out by exciting at 355 nm. The transient spectra of Al(III)salen (Figure 6) recorded in (*R*)- and (*S*)-2-butanol were very similar. They coincide with the spectra obtained in acetonitrile as well as in ionic liquids, supporting the occurrence of the same processes in every case (see step i in eq 1 above). Thus, in spite of the high fluorescence yield observed in butanols compared to the other solvents, some Al−Cl homolitic bond cleavage still occurs (obviously with considerably lower efficiency) when Al salen complex is photolyzed in butanols. Importantly, the decay of the signal monitored at 480 nm, which is characteristic of the radicaloid species, is considerably shorter lived in (*S*)-2-butanol (4.4 μs) than in (*R*)-2-butanol (18.6 μs). The lifetime of the salen Al(II) radical is of the same range as in acetonitrile. However, in 2-butanol, the main decaying process of the photogenerated salen Al(II) radical is by hydrogen abstraction from the solvent to form a metal hydride according to eq 2. In a previous work, we



have shown that this aluminum hydride can serve to enantioselectively reduce carbonyl groups.[19]

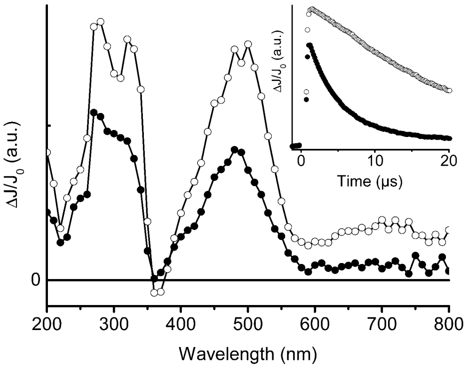


Figure 6. Transient absorption spectra of salen aluminum complex (1.3×10^{-4} M) in (*R*)-2-butanol (○) and (*S*)-2-butanol (■) recorded under N_2 4 μs after 355 nm excitation. The inset shows the decays of the Al(II) salen radical monitored at 480 nm in (*R*)-2-butanol (○) and (*S*)-2-butanol (■).

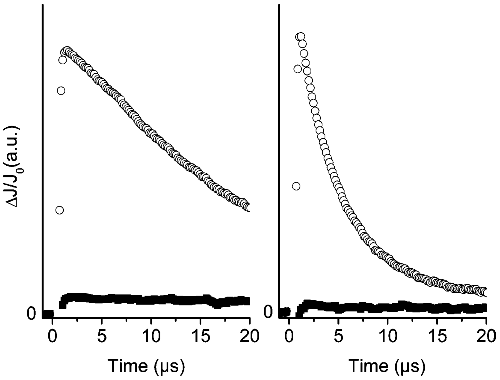


Figure 7. Decays of the signal monitored at 480 nm under N_2 (○) and O_2 (■) of the salen Al(II) radical in (*R*)-2-butanol (left) and (*S*)-2-butanol (right).

Thus, the decay of the Al(II) salen intermediate in alcohols occurs by hydrogen abstraction from the solvent, allowing the operation of asymmetric recognition of the chiral metal salen intermediate and the chiral 2-butanols. This asymmetric recognition can be clearly assessed by the difference in lifetime of the intermediate depending on the configuration of the 2-butanol asymmetric center (Figure 7). Miranda and co-workers have recently reported precedents in which chiral n,π* triplet excited states of benzophenones abstract hydrogen atoms at different rate constants depending on the configuration of chiral centers.[60−62] Upon purging under O_2, quenching of the transient absorption band assigned to the radical salen metal was observed and the temporal profile of the decay was dramatically affected (Figure 7).

Conclusions

In this work, we have shown that the photochemical behavior of a salen metal strongly depends of the nature of the solvent. Ionic liquids notably stabilize the radicaloid species generated by homolysis of the Al−Cl bond. The anion of the solvent plays a role on their polarity and viscosity and, consequently, on the lifetime of the singlet excited state of pentacoordinated salen Al(III) and also on the Al(II) radicaloid transient. This transient can decay by hydrogen abstraction from hydrogen-donor solvents like alcohols. In accordance with the wide use of chiral metal salen complexes in asymmetric catalysis, it has been observed that a high degree of diastereomeric recognition between the Al(II) transient and the configuration of the chiral solvent alcohols. These results are of interest in the context of enantioselective photochemical reactions.

Acknowledgment. Financial support by the Spanish Ministry of Science and Education (grant CTQ06-5678) is gratefully acknowledged. B.F. thanks also the Ministry of Education for a research associate contract (Juan de la Cierva).

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