ARTICULOS PUBLICADOS

QOFS: **Química Orgánica en Fase Sólida**

La productividad de esta línea de investigación en cuanto a artículos publicados durante el periodo 2012-2017 fue de 34 artículos científicos.

A continuación se da el detalle de los artículos publicados.

1) Ramirez-Herrera D. E., Tirado-Guizar A., Paraguay-Delgado F., Pina-Luis G. Ratiometric arginine assay based on FRET between CdTe quantum dots and Cresyl violet, *Microchim. Acta*, **2017**, 184 , 1-9.

2) Martínez-Quiroz, M.; López Maldonado, E. A.*; Ochoa-Terán, A.*; Oropeza-Guzman, M. T.; Pina-Luis, G. E.; Zeferino-Ramírez, J. Innovative uses of carbamoyl benzoic acids in coagulation-flocculation´s processes of wastewater. *Chemical Engineering Journal*, **2017**, 307, 981-988.

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4) Martínez-Quiroz, M.; Ochoa-Terán, A.*; Aguilar-Martínez, M.; García-Elías, J.; Santacruz-Ortega, H.; Miranda Soto, V.; Pina-Luis, G. New fluorescent metal receptors base on 4,4´-carbonyl bis(carbamoylbenzoic) acid analogues with naphthalene fluorophore. *Supramol. Chem.* **2017.** DOI: http://dx.doi.org/10.1080/10610278.2016.1277585.

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ORIGINAL PAPER

Ratiometric arginine assay based on FRET between CdTe quantum dots and Cresyl violet

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Abstract The authors report on the design of a new Förster resonance energy transfer (FRET) based ratiometric nanoprobe for the determination of arginine. The method is based on the inhibition of the efficiency of FRET in assemblies formed between CdTe quantum dots capped with mercaptopropionic acid (QD-MPA) acting as energy donor, and the dye Cresyl Violet (CV) that acts as an energy acceptor at pH 8. Addition of arginine causes a displacement of the CV by arginine on the surface of the QD/MPA. Hence, the FRET between QD/MPA and CV is interrupted and fluorescence emission of the donor (QD/MPA) is restored. Arginine selectively binds to the QD/MPA via electrostatic and hydrogen bonding interactions between guanidinium and carboxylate. Under optimum conditions, the ratio of the fluorescence emissions peaking at 575 and 620 nm (under 400 nm excitation) is linear in the 1 to 30 μM arginine concentration range, and the detection limit is 0.51 μM. The nanoprobe displays good selectivity over 14 other amino acids, many metal ions, glucose, and ascorbic, tartaric and citric acids. The fluorescent nanoprobe was successfully applied to the determination of arginine in pure and spiked real samples and gave good recoveries. Its good selectivity, sensitivity, low-cost and rapidity make the QD-dye assembly a suitable nanoprobe for the quantitation of arginine.

Keywords Arginine determination · Quantum dots-dye assemblies · Quantum yield · Salt bridge guanidinium-carboxylate · Energy transfer nanoprobe · Förster resonance energy transfer

Introduction

A main challenge in analytical chemistry is to develop fast, specific, and sensitive sensors for food, clinical and environmental applications. Förster resonance energy transfer (FRET) mechanism has been widely studied as a powerful and promising sensory tool for detection and quantification of analytes of biological and chemical interest. FRET is a non-radiative process in which the electronic excitation energy of a donor (usually a fluorophore) is transferred to a ground state acceptor via dipole-dipole interactions [1]. Colloidal quantum dots (QD) are one of the most interesting new materials that have emerged over the last decades, their optical and spectroscopic properties allow their use as fluorescent labels for sensing and bioimaging applications [2–4].

QD properties also offer new opportunities and special advantages in FRET assemblies as they can improve energy transfer efficiencies, facilitate the design of donor-acceptor configurations, and simplify quantitative measurements. Some of the advantageous properties of using QD as FRET energy donors are: broad absorption spectra, this allows selecting an excitation wavelength in which acceptor absorption is minimal, size-tunable fluorescence emission with high quantum yields

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Innovative uses of carbamoyl benzoic acids in coagulation-flocculation's processes of wastewater

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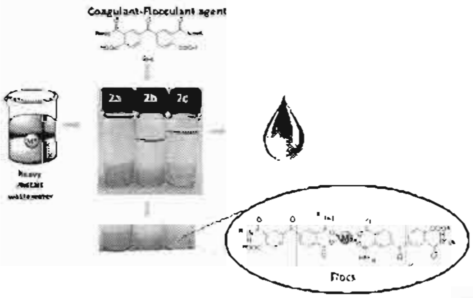
HIGHLIGHTS

- Carbamoyl benzoic acids were tested as separation new agents for wastewater.
- Zeta potential is a powerful tool to evaluate new products for wastewater treatment.
- Integration of supramolecular chemistry to heavy metals removal as a new alternative.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of carbamoyl benzoic. acids as separation new agents, to remove on the hazardous heavy metals, that are frequently, contained in metal plating wastewater is reported in this paper. The interaction of ionic heavy metals and carbamoyl benzoic acids was studied approaching zeta potential in aqueous solutions. These carbamoyl acids are innovative chemicals that demonstrate their potential to bind metallic ions as Pb^{2+}, Cu^{2+} and Hg^{2+} under specific physicochemical conditions (pH solution and metal–ligand relationship). The amide substituent in each compound induced a specific affinity toward the metallic ions contained in water, and it was studied by measuring zeta potential of an inert surface in contact with the aqueous media. This measurement allowed us to determine the association constants (K_f) with metal ions after defining the stronger interaction between the carbamoyl acids and metallic cations. These results suggest that coagulation-flocculation process could be expected for Pb^{2+} over all the studied metals (Cu^{2+}, Hg^{2+}, Ca^{2+}, Fe^{2+}, Ni^{2+}, Mg^{2+}, Ba^{2+}, Al^{3+} and Cd^{2+}). The order of effectiveness of the carbamoyl acids for the separation of Pb^{2+} is b > c > a according to substituent and the calculated values of K_f which match the observed behavior. To corroborate the practical use of carbamoyl acids as coagulants. Sedimentation and clarification kinetics were analyzed with transmittance measurements versus time. Coagulation-flocculation test was validated by SEM-EDS analysis.

1. Introduction

Water quality assessment is done through a series of tests designed to quantitatively and qualitatively determine the most

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Copper nanoclusters-coated BSA as a novel fluorescence sensor for sensitive and selective detection of mangiferin

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ABSTRACT

In this paper we report for the first time a fluorescence nanosensor for the detection of trace amount of mangiferin (MGF) by using bovine serum albumin (BSA)-protected copper nanoclusters (CuNCs@BSA). The CuNCs@BSA have an average size of 1.4 ± 0.2 nm and show a blue emission at 640 nm. Fluorescence emission of CuNCs@BSA was quenched in the presence of MGF providing a fluorescence responsive probe in a linear range of 3–180 μM with a detection limit of 210 nM calculated at a signal-to-noise ratio of 3. The CuNCs@BSA show high photostability, since after 50 min of irradiation, only a fluorescence decrease of 15% is appreciated. Interference and competition studies indicate that the nanoprobe presents good selectivity over other relevant molecules including flavonoids and metal ions. These results confirmed that the nanosensor has high selectivity towards MGF in the presence of other substances. In addition the mechanism of sensitive fluorescence quenching response of CuNCs@BSA to MGF has been discussed. The sensor was then applied to the analysis of MGF in African mango extract and satisfactory recoveries were obtained indicating a good accuracy and reproducibility of the fluorescence nanosensor for detection of MGF. The proposed sensor is simple, rapid, and cost-effective demonstrating great potential for the determination of MGF in real samples.

1. Introduction

Flavonoids are polyphenols formed of three phenolic rings. They can be found normally in fruits and vegetables [1,2]. Mangiferin (MGF) (Fig. 1) is one flavonoid with glycosylated structure (2-β-D-glucopyranosyl-1,3,6,7-tetrahydroxy- 9H-xanthen-9-one), which is commonly found in fruits, leaves, stem bark and root of *Mangifera indica* [3,4]. Due to its powerful antioxidant and antiradical activity, MGF has received considerable attention because of its multiple biological and pharmaceutical applications, such as, antiviral, anticancer, antidiabetic, anti-HIV, anti-inflammatory and protector against cardiovascular diseases [5,6]. The MGF can be found in a variety of mangoes and extracts of this substance are prepared to attend medical issues like diabetes [7] and cancer [8].

Owing to the bioactive and pharmacological importance of MGF, the development of robust, sensitive and fast methods for MGF determination in various types of samples is of great interest. Several techniques have been used to investigate the determination of MGF and other flavonoid compounds, such as high performance liquid chromatography [6,9], capillary electrophoresis [10,11] and electrochemical techniques [3]. Although HPLC method has good resolution for the detection of flavonoid compounds, it is still quite costly and often requires of complicated procedures. Alternatively, electrochemical methods are simpler and less costly procedure in comparison to HPLC but can suffer from interference of coexisting substances.

Fluorescent methods have not been widely used in the MGF detection. As it is known this method is sensitive, simple and inexpensive, and can determine concentrations to trace levels [12]. In this type of sensor, the signaling unit may consist of fluorescent organic molecules [13,14] or more recently have been

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New fluorescent metal receptors based on 4,4′-carbonyl bis(carbamoylbenzoic) acid analogues with naphthalene fluorophore

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ABSTRACT

In this manuscript is described a research related with two ditopic receptors based on 4,4′-carbonyl bis(carbamoylbenzoic) acids bearing a naphthyl (**2a**) and naphthylmethyl fluorophores (**2b**), which interact with metal ions. The fluorescence properties of both receptors were influenced by the connectivity with the amide group. The non-spaced receptor **2a** presents an electron delocalisation from the amide to the naphthyl group having a broad red-shifted emission band and high quantum yield. The spaced receptor **2b** presented a photo-induced electron transfer (PET) process from the amide to the naphthyl group, and a structured emission band is present at the UV region with low quantum yield. The different chemical structure influenced the fluorescent response used to analyse the coordination with metallic ions. The **2a** receptor has an *ON–OFF* response because of the inhibition of the ICT process. The **2b** receptor shows an *OFF–ON* response because of the inhibition of the PET process. Additional analytical studies by ^{1}H-NMR and FTIR demonstrated the strong interaction of the amide and carboxylic functional groups with the metallic ions. Competitive experiments with EDTA showed that a very stable complexes are obtained between metallic ions and the new receptors.

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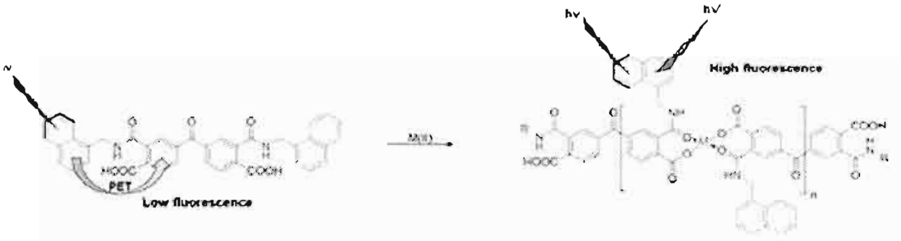

Introduction

The development of synthetic hosts for cations is one of the most active research fields of supramolecular chemistry (*1*). Fluorescent chemosensors have received considerable attention due to their potential use in biological and environmental fields (*2–13*). Among diverse fluorescent receptors the naphthalene 4,4′-carbonyl bis(carbamoylbenzoic) acids have attracted our attention by reason of their fluorescent properties and photo stability. As far as we know, there are no reports in literature about any supramolecular study of their interaction with metal ions base on the fluorescent properties of bis(carbamoylbenzoic) acid derivatives. Lingaiah et al. reported the coordination of monotopic ligands as 2-(aminocarbonyl)benzoic acid, 2-(phenylaminocarbonyl)benzoic acid, 2-(2-aminophenylaminocarbonyl) benzoic acid and 2-(2-naphthaleneaminocarbonyl)benzoic with Cu(II) ions (*14*). In this study, the metal–ligand ratio was reported (1:2) and established an interaction between ligands and metal centre through a metal-heteroatom ionic bond with the carboxylate group and a coordination bond with the amide carbonyl group. More recently, Pirrung et al. reported the combinatorial synthesis of catalytic peptoids from secondary amines with aliphatic and aromatic anhydrides capable of complexing with metal cations by carbamoylbenzoic acid functional

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Communications

An easy one-step synthesis of imidazolin-2-ones from phthalic anhydrides and their antioxidant evaluation

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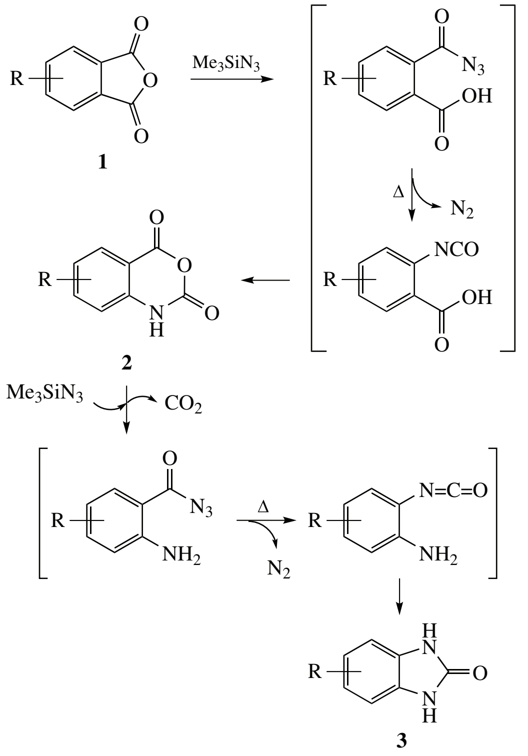
Treatment of phthalic anhydride derivatives with trimethylsilyl azide affords benzimidazolin-2-ones in 45–91% yield, which is the result of two consecutive Curtius reactions. Within the series obtained, 1,3-dihydro-2*H*-imidazo[4,5-*b*]pyridin-2-one showed highest antioxidant activity.

Imidazolidinones are commonly synthesized by cyclization of 1,2-diamines with phosgene or 1,1′-carbonyldiimidazole.[1] For the synthesis of imidazolidinones several routes have been reported,[2] but probably the most commonly used methodology involves the use of isocyanates, *i.e.*, the reaction with amino alcohols,[3] amines,[4] α-imino ketones,[5] vinylaziridines[6] and allylamines.[7] Imidazolidinones are found in several natural compounds, *e.g.*, Biotin (vitamin B) which was isolated from yolk, and is a coenzyme in the carboxylation reaction in the biosynthesis of the fatty acids.[8] Imidazolidinones have been reported against β-secretase (BACE1) inhibitors in Alzheimer's disease,[9] $\alpha_v\beta_3$-antagonist in the prevention and treatment of Osteoporosis,[10] against *Schistosoma mansoni*,[11] selective Human Enterovirus 71 inhibitors,[12] muscarinic M3 selective antagonists.[13] They possess anticancer (A549, COLO205, KATO III, K562),[13(*c*)] antibacterial and antifungal,[14] and antileishmanial[15] activities.

Recently, we have reported the synthesis of small heterocyclic compounds and their antioxidant evaluation.[16] Currently, our research is focused on the development of a simple one-pot synthesis of small heterocyclic compounds with potential biological activities. In this paper, an easy one-step synthesis of benzimidazolin-2-ones from phthalic anhydride derivatives with trimethylsilyl azide (TMSA) and their antioxidant evaluation are reported.



Scheme 1

On the treatment of phthalic anhydrides **1** with TMSA the Curtius rearrangement leads to benzoxazine-2,4-dione intermediates **2**, followed by the second Curtius rearrangement and final intramolecular cyclization to provide imidazolin-2-ones **3** (Scheme 1). We started with the optimization of reaction conditions using phthalic anhydride **1a** as a model. First, a comparison between the reaction efficiencies of TMSA generated *in situ* and commercial reagent was made with TLC monitoring until the reaction of the phthalic anhydride was complete. The reactions of TMSA generated *in situ* (from trimethylsilyl chloride with sodium azide) and commercial reagent in THF for 30 h at reflux provided compound **3a** in 20 and 51% isolated yields, respectively. Subsequently, different solvents [DMSO, benzene, acetonitrile and benzene–acetonitrile (3:1 v/v)] were tested under optimal reaction conditions. When DMSO was used as a solvent, product **3a** was not formed and some non-identified by-products were obtained. Probably this reaction follows a mechanism similar to that proposed by Snyder[17] for the synthesis of alkyl chloride from TMSCl. In contrast, the employment of other above solvents favored the expected product but gave a lower yield than THF. Note that the matched conditions do not require any sophistication and can be readily accomplished. The solvent was evaporated *in vacuo* and the product precipitated with diethyl ether, to provide the corresponding imidazolin-2-ones in moderate to good yields. The highest yield in THF could be associated with the solubility of reagents and intermediates in this solvent. The yields of imidazolin-2-ones **3a–g** synthesized using this methodology (Table 1)[†] were 45–91% depending on the structure of the starting material. The structures of the imidazolin-2-ones were confirmed by NMR, IR spectra, and GC-MS. Jones and Schofield[18] reported the synthesis of imidazolin-2-one by a four-step method from 1,2,3,6-tetrahydrophthalic anhydride with TMSA in 72 h to give a 19% of overall yield but obtained a mixture of imidazolin-

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Water-compatible core–shell Ag@SiO_2 molecularly imprinted particles for the controlled release of tetracycline

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ABSTRACT

Silver nanoparticles coated with molecularly imprinted silica shell (Ag@SiO_2-MIP) were synthesized, and their properties for the molecular recognition and the controlled delivery of tetracycline (TC) in aqueous environments were investigated. In this study, a synthesis protocol based in the entrapping of TC into silica particles with a core of silver nanoparticles (AgNPs) was developed. These particles were examined by transmission electron microscopy, scanning electron microscopy, energy dispersion spectroscopy, Fourier transform infrared spectroscopy, zeta potential and UV visible, and fluorescence spectroscopy. The as-prepared Ag@SiO_2-MIP particles were evaluated for selective recognition of TC. The imprinted particles have higher TC binding ability as compared with corresponding non-imprinted particles and have high selectivity toward TC over other competitive antibiotics. The studies of release profiles of TC-loaded Ag@SiO_2-MIP particles in aqueous solutions demonstrated a strong dependence with pH and temperature. The kinetic delivery of TC showed two types of release which includes initial burst release (low-affinity sites) and slow release (high-affinity sites). The amount of TC release from Ag@SiO_2-MIP particles was lower at pH 2 (simulated gastric fluid) to pH 8 (simulated colonic fluid), which makes the proposed system a good candidate for TC oral administration. The excellent biocompatibility of the silica materials, the known bactericidal properties of the AgNPs, and the drug release results render the possibility of designing a new generation of TC delivery systems for controlled release.

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Flavone functionalized magnetic nanoparticles: A new fluorescent sensor for Cu^{2+} ions with nanomolar detection limit

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ABSTRACT

This paper presents the preparation and characterization of a new class of fluorescent core-shell magnetic nanoparticles composed of a Fe_3O_4 core, coated with amino-functionalized silica shell and modified with morin (Fe_3O_4@SiO_2-NH_2-morin). These nanoparticles were examined by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), zeta potential and vibrating sample magnetometer (VSM). The fluorescent magnetic nanoparticles were analyzed by UV–vis and fluorescence spectroscopy. The characterization data showed that the nanoparticle diameter is increased at each synthesis step (from 14 to 78 nm) and that all nanoparticles have superparamagnetic properties. The fluorescence response of morin-magnetic nanoparticle towards Cu^{2+} ions showed a significant and selective fluorescence quenching. Morin functionalized magnetic nanoparticle are found to be highly selective for Cu^{2+} ions whereas the interference from other metal ions and biological compounds was negligible. The nanosensor not only provided a sensitive (7.5 nM) and selective detection of Cu^{2+} ions, but a new fluorescent and biocompatible material with potential use in biological applications.

1. Introduction

Magnetic nanoparticles have demonstrated potential applications in catalysis, cell labelling, drug delivery, contaminant separation and other owing to their magnetic features [1–11]. In particular, sensors based on magnetic nanoparticles have attracted considerable interest due to the significant improvement in sensitivity and selectivity that can be achieved by this method. Core-shell nanoparticles consisting of a magnetically responsive core and a silica shell have some important advantages. First, the magnetic core makes them easy to separate and recycle from matrix with an external magnet. Second, they are biocompatible and have greater stability. Furthermore they are readily synthesized by sol–gel method and easily modified by a wide range of functional groups including thiol, amine, and carboxylate groups [12–15]. These functional groups provide sites for surface modification with various chemical and biomedical ligands. The thick silica layer can act as the support of fluorescent probes to develop non-toxic, biocompatible, and recoverable fluorescence nanosensors.

Morin (3,5,7,2′,4′-pentahydroxyflavone) is a polyphenolic compound derived from flavones (Fig. 1) that possesses a wide range of bioactivities and is often employed as anti-inflammatory, antioxidant, antineoplasic and as cardiovascular protector agent [16,17]. It has the ability to form complexes with some metal ions and can act as an excellent scavenger of metal ions from contaminated samples. Modification with morin provides fluorescent properties to the nanoparticle and serves as a biocompatible receptor friendly to the environment useful in the recognition and separation of metal ions, as effective metal chelating agent and in many biological applications.

Morin has been immobilized on different supports and successfully employed in the separation and preconcentration of trace metals [18–20] but to our knowledge, there are no reports on the use of morin immobilized on the magnetic nanoparticle as material for the recognition of heavy metals. In particular the design of a Cu^{2+} ions sensor has received attention given its implications in a number of neurodegenerative diseases as well as ecological pollution. Copper trace ions are vital in various enzymatic processes; its deficiency may lead to several neurological problems. On

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Photoinduced electron transfer in *N*,*N*-bis(pyridylmethyl)naphthalenediimides: study of their potential as pH chemosensors

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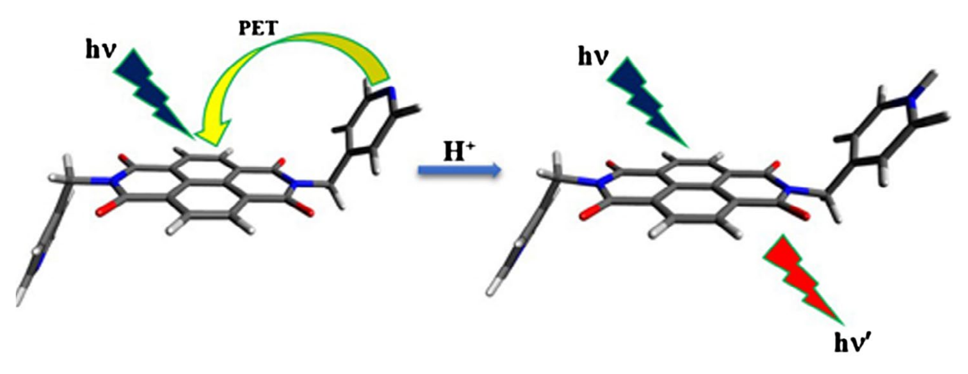
ABSTRACT

The change in fluorescent properties of a series of *N*,*N*-bis(pyridylmethyl)naphthalenediimides (BIPy-NDIs) as function of pH were investigated. The naphthalenediimide dyes displayed *OFF–ON* pH sensing properties owing to photoinduced electron transfer in the pH range from 1.7 to 4.1. The fluorescence enhancement of the chemosensors studied is based on the hindering of photoinduced energy-electron transfer (PET) from pyridine ring to the naphthalene fluorophore by protonation. Moreover, using density functional theory theoretical calculations of molecular orbitals, it was verified that protonation nitrogen atom in pyridine ring inhibits the PET process. The best selective response for monitoring pH in the presence of different metal ions, was exhibited by BIPy-NDI **1B**. In addition, **1B** was applied for determination of pH in real samples of commercial vinegars. The results were consistent with those obtained by glass electrode method, indicating that the new probe could be a practical pH indicator in strongly acidic conditions.



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KEYWORDS
N,*N*′-bis(pyridylmethyl) naphthalenediimides; PET; pH chemosensor

Introduction

Naphthalenediimides (NDIs) are a class of compounds that have become increasingly important in the last decade, with a series of applications ranging from the biomedical to material science due to their outstanding photo- and electrochemical properties (*1*). NDIs are excellent materials for studying electro- or photoinduced electron transfer reactions and can be incorporated into larger multi-component assemblies such as field effect transistors, biological models and supramolecular devices (*2*). They are excellent electron acceptors in aqueous solution and ideal for the design of synthetic derivatives that can be used as structural probes and therapeutic agents in molecular biology and chemotherapy (*3–5*). NDIs have been used to reduce and oxidise proteins (*6–8*) and DNA (*9–11*). Most studies in aqueous solution involve the binding to nucleic acids and many of these derivatives are used as DNA intercalators (*7–11*). They also show biological applications rely mainly on their pharmacological activity as local anesthetics (*12, 13*), tumoricidals (*14, 15*) and antivirals (*16–18*).

Photophysical characterisation of NDIs is limited to a few derivatives mainly due to their low solubility in aqueous media. However, İçli and co-workers (*19*) reported the photoinduced energy-electron transfer (PET) in NDIs and demonstrated that electron donor groups in the *N*-substituent of the NDI quench the fluorescence emission.

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Colorimetric and Fluorescent Determination of Fluoride Using a Novel Naphthalene Diimide Boronic Acid Derivative

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Colorimetric and Fluorescent Determination of Fluoride using a Novel Naphthalene Diimide Boronic Acid Derivative

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Abstract

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Novel naphthalimide–aminobenzamide dyads as *OFF/ON* fluorescent supramolecular receptors in metal ion binding

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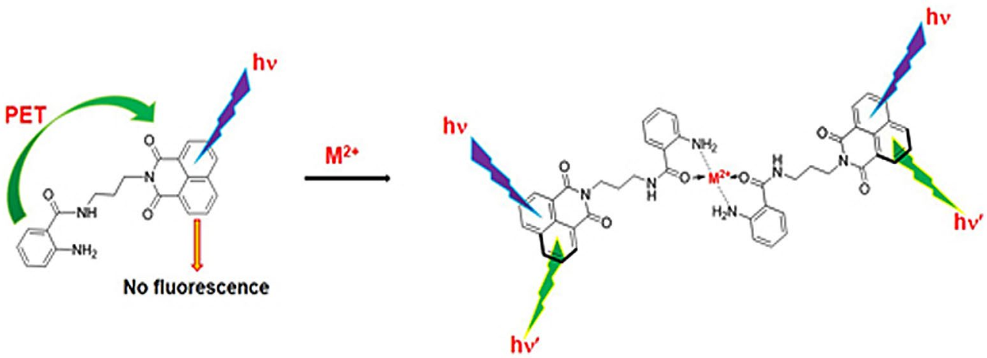
ABSTRACT

A series of novel naphthalimide–aminobenzamide (NAPIM-2ABZ) dyads **3** connected by different length polymethylene chains were synthesized and studied as fluorescent supramolecular receptors in metal ion binding. The photophysical properties were evaluated and compared with separated chromophores. The electronic absorption spectra of dyads **3** showed no interaction between chromophores in the ground state. The fluorescence quantum yields were lower in dyads **3** in comparison with *N*-propyl-2-aminobenzamide (**8**). The fluorescence quenching is attributed to a PET mechanism between fluorophores (from 2ABZ to NAPIM), which is dependent on the polymethylene chain length. In metal binding study was found a response towards transition metal ions such as Hg(II), Cu(II), Zn(II) and Ni(II). Dyad **3b** presented selectivity towards Cu(II). The UV-vis, IR and ^{1}H-NMR studies demonstrated the interaction with 2ABZ moiety in the ground state, and interestingly dyads with shorter polymethylene chains **3a** (*n* = 0), **3b** (*n* = 1) and **3c** (*n* = 2) exhibited an *OFF/ON* fluorescence behaviour due to the PET inhibition and the quenching of 2ABZ fluorescence. Dyads **3d** (*n* = 4) and **3e** (*n* = 6) presented opposite response *ON/OFF* in the complex with metal ions evidencing the absence of PET in these dyads.



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KEYWORDS
PET; dyads; naphthalimide; aminobenzamide; metal binding

Introduction

2-Aminobenzamide (2ABZ) has been extensively studied as fluorescent label in order to improve the oligosaccharide detection and sequencing by high-performance liquid chromatography (*1–6*). The introduction of 2ABZ as fluorescent probe into saccharides occurs through a two-step reductive amination. The same strategy has been used in the label of monosaccharides with *N*-aminoethyl-2-aminobenzamide (2AEAB) (*7*), which has the advantage of being a bifunctional molecule and allows to develop microarrays to study the protein–carbohydrates interactions (*8*). Fluorescent sensors for the detection of Zn(II) with a 2ABZ moiety as fluorophore were reported (*9, 10*).

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Electrochemical and Spectrometric Studies for the Determination of the Mechanism of Oxygen Evolution Reaction

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A novel study of the oxygen evolution reaction (OER) mechanism at different anode materials is shown using the two approaches: electroanalytical and spectroscopic. For first time, new evidence is provided for electroanalytical approach which consists of using chronoamperometric curves, to obtain Tafel plots at different detection times. Besides, intermediates of OER (e.g. $^{\bullet}OH$) were detected and quantified indirectly by fluorescence spectroscopy. This technique detects the formation of 7-hydroxycoumarin in situ from the reaction between coumarin and $^{\bullet}OH$. Among all anode materials tested, only SnO_2-Sb_2O_5 and boron doped diamond (BDD) electrodes showed the typically Tafel slope value of 120 mV dec^{-1}, associated with a primary water discharge as determining step, where $^{\bullet}OH$ is the main active intermediate. The potential that provide the best detection of $^{\bullet}OH$ in several electrolytes for these two electrodes were identified. This spectroscopic studies support the evidence of the formation of $^{\bullet}OH$ as the rate determining step (RDS) in the OER mechanism.

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In recent years, electrochemical research has mostly focused on pollutant degradation, evaluating different electrochemical methods,[1–4] and process designs[5] to remove trace amounts of organic compounds in wastewater. Among the several electrochemical methodologies reported, electrochemical oxidation has provided a path to total mineralization of pollutants.[6] However, this process strongly depends on the both the medium being treated and electrode materials chosen for their ability to form strong oxidants.[7] Among the known oxidant species, $^{\bullet}OH$ has attracted much attention because of its high oxidizing power, which is a highly desirable feature for the destruction of toxic organic contaminants.[8] In addition, $^{\bullet}OH$ is well recognized as potent reactive oxygen species in biological systems which is known to cause oxidative stress and other physiological complications in living organisms. Therefore, numerous researchers have reported on the $^{\bullet}OH$ generation.[8–11] Methods for $^{\bullet}OH$ generation includes Fenton or Electro-Fenton process,[12] radiation of TiO_2 photocatalyst in aqueous media,[9] and polarization at high anodic potentials.[13] Consequently, polarization at high anodic potentials can lead to mineralization of organic compounds via electrochemical oxygen transfer reaction (EOTR). However, the determining step of EOTR can be attributed to anodic discharge of $^{\bullet}OH$ to O_2 in the oxygen evolution reaction (OER).[13]

OER is an anodic process in which oxidation of water takes place via the transference of either one electron, leading to the electrogeneration of $^{\bullet}OH$ (Reaction 1) or involving two transferred electrons, leading to oxygen evolution (Reaction 2) and production of less powerful oxidants such as O_2, O_3, etc.[14]

$$H_2O \rightarrow \cdot OH + H^+ + e^- \qquad [1]$$

$$H_2O \rightarrow \frac{1}{2}O_2 + 2\,H^+ + 2\,e^- \qquad [2]$$

The rate of OER at given electrode potential depends critically on the nature of electrode materials.[15] PbO_2,[14,16] SnO_2-Sb_2O_5[17] and boron-doped diamond (BDD),[18] are anode materials reported with high overpotentials for oxygen evolution. On the other hand, platinum based-electrodes[19] and dimensionally stable anodes (DSA)[20,21] are electrodes reported with low overpotentials for oxygen evolution. OER is a complex process and is not only a function of overpotential value due to the possibility of different pathway occurring simultaneously. This process depends on several thermodynamics parameters such as electrolyte, temperature, anode material, electrolyte concentration, etc. A large number of reports discuss the mechanistic aspects of OER in terms of Tafel slope values.[11,13,15,19] The discussion of this reaction mechanism of OER is mostly based on the analysis of Tafel slope value, supplemented by spectroscopic studies of the nature of the reaction intermediates.[15]

Several mechanisms differing in molecular details have been proposed for OER.[15,19,21] A generalized mechanism can be stated as follows:

$$S + H_2O \rightarrow S - \cdot OH + H^+ + e^- \qquad [3]$$

$$S - \cdot OH \rightarrow S - OH \qquad [4]$$

$$S - OH \rightarrow S - O + H^+ + e^- \qquad [5]$$

$$2S - O \rightarrow O_2 + 2S \qquad [6]$$

The first step of the generalized mechanism is the discharge of water (Reaction 3) with the generation of S-$^{\bullet}OH$ which is the main active intermediate of OER. Depending on the nature of the electro material, a surface rearrangement of the $^{\bullet}OH$ could take place resulting in a more stable specie, (Reaction 4). This stable specie is susceptible to electrochemical oxidation (Reaction 5), and subsequently oxygen is released (Reaction 6). Thus, the rate determining step (RDS) of OER mechanism is related to Tafel slope value.[22]

A large number of publications report the Tafel slopes from different materials and electrolytes using linear sweep voltammetry,[10,11,13,20,23] or galvanostatic polarization.[22] Tafel slope values are usually between 30 to 120 mV dec^{-1}.[15] Table I summarizes the Tafel slope values founded in literature for OER. The intermediate Tafel slope values are interpreted in terms of mixed mechanism or of intermediate coverage with adsorbed species,[15] and this phenomenon is associated with the surface rearrangement as the RDS (transformation of the intermediate). Nevertheless, Tafel slope values higher than 120 mV dec^{-1} may result from the presences of species adsorbed that act as barrier for OER,[11] this fact is related with the formation and adsorption of S-$^{\bullet}OH$ as RDS.[22] Multiple Tafel slopes can also be observed as function of overpotential where the transitions can be due to (a) changes in the coverage of adsorbed species for the same RDS of the same mechanism, (b) changes in the RDS in the same mechanism, and (c) changes in the mechanism.[15] Under the basis of a generalized mechanism, only changes in the adsorbed species or changes in the RDS are considered for further discussion.

The physicochemical properties of $^{\bullet}OH$ makes it possible for these radicals to carry out the mineralization of organic contaminants. However, the concentration of $^{\bullet}OH$ is difficult to quantify due to a highly active intermediate and a lifetime of approximately 10^{-9} s.[31] Since

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Catalytic Synthesis of Hydantoins Derivatives by Pulsed Fe electro-oxidation 110396

By IA Rivero

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Catalytic Synthesis of Hydantoins Derivatives by Pulsed Fe electro-oxidation

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This paper presents an innovative green organic electrochemical/chemical (EC/C) synthesis to prepare hydantoins from *N*-Alkyl-piperidin-4-ones and compare it with the traditional Bucherer-Bergs method. The main characteristic of this proposal is the *in-situ* production of F[illegible]I) by the electro-oxidation of Fe° serving as catalyst in the synthetic path of hydantoin. Products were characterized by IR, NMR (^{1}H, ^{13}C), and MS. The pulsed application of 0.9V/Ag/AgCl/Cl$^{-}_{\text{sat KCl(MeOH)}}$ with rest potentials of -0.1V/Ag/AgCl/Cl$^{-}_{\text{sat KCl(MeOH)}}$ were found to be the optimal conditions, given the highest charge values: 2.68C/cm^{2} for **2b**, and 5.57C/cm^{2} for **2a**, after 10 cycles (60min). The EC/C synthesis was compared with Bucherer-Berg method, and resulted in an increase of 12-fold more hydantoins in 60min. The salts own used in the reaction (KCN and $(NH_4)_2CO_3$) dit not required common addition of TBATFB tetrabutilammonium tetrafluoroborate (TBATFB) and tetrabutilammonium hexafluorophosphate (TBAHFP), it was necessary for to carry out the electro-synthesis process. Products were characterized by IR, NMR (^{1}H, ^{13}C), and MS. The success of the electrochemical assisted synthesis was compared with the traditional Bucherer-Bergs method previously reported.

Keywords: hydantoins, N-piperidone, Fe electro-oxidation in metanol-water, organic electrochemical/chemical synthesis.

1. INTRODUCTION

The application of electrochemical techniques in organic synthesis has become a tool in its improvement, turning out to be innovative and attractive to traditional methods. The process involves the transferring electrons from a heterogeneous electrode to adsorbed compounds in its surface [1,2,3], also, since only electric current is applied, which might even originate from renewable resources, no

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In-situ Fe electro-oxidation to Improve the Synthesis of Mono and Disubstituted Benzimidazoles

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This paper presents an innovative green organic electrosynthesis to prepare benzimidazoles in methanol media at room temperature starting from *o*-phenylendiammines and benzaldehydes. The main characteristic of this proposal is the *in-situ* Fe electro-oxidation serving as catalyst in the synthetic path of benzimidazoles mono and disubstituted. Anodic linear sweep voltammetry of Fe wire in methanol were used to select the supporting electrolyte among tetrabutilammonium tetrafluoroborate (TBATFB) and tetrabutilammonium hexafluorophosphate (TBAHFP). I vs. E plots pointed toward TBATFB as a better supporting electrolyte due to the fact that Fe presents a lower potential dissolution compared with TBAHFB. Electrolysis at constant potential was performed in a three-electrode undivided cell to prepare two different benzimidazoles (mono and disubstituted) using 1mM TBATFB in methanol. In both cases, good yields and easy purification were achieved. Results indicate that *in-situ* soft electrochemical Fe oxidation produce fresh Fe(III) to act as an effective catalyst for benzimidazoles synthesis and succeed a green chemistry process. Products were characterized by IR, NMR (^{1}H, ^{13}C), and MS. The success of the electrochemical assisted synthesis was compared with a $FeCl_3$/Alumina previously reported.

Keywords: benzimidazole, *o*-phenylenediamine, Fe electro-oxidation in methanol, organic electrosynthesis

1. INTRODUCTION

Electro-organic synthesis and organic electrosythesis have been considered as promising approaches to prepare more than a few organic compounds [1]. The most common procedures are the direct electrochemical reaction of some of the reagents, corresponding to electro-organic synthesis.

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Fluorescence enhancement study of shell-less CdTe quantum dots

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ABSTRACT

We report a systematic study on the synthesis of shell-less CdTe quantum dots towards the enhancement of their luminescence properties. Reaction times and Cd:Te molar ratios were investigated to optimize the synthesis conditions. It was found that these parameters have a significant influence on the quantum dots emission wavelengths and photoluminescence quantum yields. The synthesis can be carried out without the use of an inert atmosphere and pyrophoric ligands in less than an hour. Water-soluble CdTe quantum dots were also prepared by modification of CdTe/ODE with mercaptopropionic acid. Hydrophobic and water-soluble quantum dots were characterized by UV-visible absorption spectroscopy, fluorescence spectroscopy, transmission electron microscopy, and energy dispersive X-ray spectroscopy. The optical stability of hydrophobic and hydrophilic quantum dots was tested irradiating the sample with a high power xenon lamp. After 45 min of illumination the hydrophobic-materials showed an excellent stability (bleaching $< 10\%$) and the hydrophilic-materials a non-reversible photo-enhancement process. After 15 minutes of stopping the illumination, the quantum yield of hydrophilic quantum dots in aqueous solution was stabilized to 55%. The characteristics of the synthesized quantum dots make them suitable for use as biological fluorescent markers, photocatalytic materials with high performance and new materials for solar cells.

Keywords: Quantum Dots, High Quantum Yield, Shell-Less, Photostability, Enhancement.

1. INTRODUCTION

Nanocrystalline semiconductors have attracted considerable attention because of their special electrical and optical properties, such as narrow emission bands, wide excitation bands, large Stokes shifts, high brightness and photochemical stability. This type of nanomaterial can be considered with great potential for biological applications in cells and tissue labeling,(1–3) bioimaging,(4) optoelectronic(5, 6) and drug delivery.(7) Among II–VI type semiconductor compounds, CdTe presents much interest because it is a material suitable for emitting in the visible and in the near-infrared (NIR) spectral range by controlling the nanoparticle size.

An important strategy in the development of new fluorescent probes is the use of quantum dots, due to their above-mentioned properties. The high surface to volume ratio of the nanomaterial and its great dispersivity provide large adsorptive surface that increase the interaction between the nanoparticle and the analyte. As a result, sensors with better selectivity and sensitivity are obtained. Moreover the fluorescence signal also offers many advantages over other detection system. It has been reported analytical probes based in fluorescence detection that allow the determination of analyte in femtomolar concentrations (10^{-15} M).(8)

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Ecofriendly synthesis of ultra-small metal-doped SnO_2 quantum dots

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Abstract

An ecofriendly synthesis is established to obtain ultra-small SnO_2 nanoparticles (NPs) doped with metals by a hydrothermal method using only tin tetrachloride, urea, and water as reagents. This synthesis was done in a short period time at low temperature and without surfactants. Microscopy analysis revealed the formation of doped tin oxide NPs with a diameter smaller than 2.8 nm. Un-doped and doped tin oxides were obtained with a tetragonal type rutile structure with an average surface area of 348 m^2/g.

Introduction

Current research groups dedicated to the area of materials science have drawn interest in luminescent materials such as quantum dots (QDs). QDs are colloidal nanocrystalline semiconductors with special luminescent properties with relatively spherical morphology, narrow emission bands (typically 20–30 nm full-width at half-maximum intensity) and high photochemical stability.[1] Luminescent QDs have great applications in light-emitting diodes,[2] biological imaging,[3] and sensors.[4]

Tin oxide (SnO_2) is a great semiconductor material with an exciton Bohr radius of approximately 2.7 nm.[5] In particular, SnO_2 has been widely used as gas sensors for monitoring the environment and as catalysts.[6] For these types of applications, small size particles and large surface area are necessary to high performance.

Doping SnO_2 nanoparticles (NPs) with small quantities of metals can improve the optoelectronic properties such as photoluminescence and optical band gap which would result in surface modification providing excellent electric properties and photocatalytic activities.[7] In particular, Zn–SnO_2 NPs have been demonstrated to be great materials for improved power conversion efficiency in Dye-sensitized solar cell.[8] Additionally dilute magnetic semiconductors produced by doping transition metal ions into non-magnetic semiconductors are of interest for potential applications in spin electronics.[9] Doped QDs also have been used as fluorescence sensors; Mn-doped ZnS QDs was used for the determination of 4-nitrophenol by QD fluorescence quenching.[10] Metal-doped SnO_2 has also been studied to developed luminescent NPs,[11] obtaining particles with sizes between 7.1 and 16.2 nm without an optical shirt on their emission wavelength.

As can be seen from the above, the synthesis of doped semiconductors is of great interest for their potential applications in various areas. In particular, there are few reports of its use as photoluminescent sensors. Therefore, the synthesis of doped SnO_2 QDs is an important topic in groups dedicated to optical materials. SnO_2 NPs have been synthesized by various methods, such as combustion,[12] laser ablation,[13] spray-pyrolysis,[14] and hydrothermal.[15] However, these methods usually need of special equipment, a high-cost, and complicated process. Each method used for SnO_2 can provide many NP morphologies with different surface areas; depending of these morphologies SnO_2 has been used for applications in field emissions,[16] solar cells,[17] rechargeable Li batteries,[18] and sensors.[19]

As mentioned above, hydrothermal synthesis has been reported; however, the synthesis conditions can be optimized. For example, SnO_2 NPs have been obtained with temperatures about 180°C with prolonged reaction times,[20] in another report a hydrothermal process involving hydrazine hydrate instead of NaOH has been used to produce SnO_2, but still using high temperatures and long periods of synthesis.[21]

In this work, we present a simple and green method for the synthesis of very small SnO_2 NPs. The synthesis does not require high temperatures, organic solvents, or surfactants making it an environmental friendly method. We developed Zn, Fe, Co, Ti-doped SnO_2 NPs, in a 6 h reaction with about 2 nm crystalline particle size.

Experimental

Synthesis method

Doped and un-doped SnO_2 NPs were synthesized following a modified methodology describe by Ye and co-workers.[22] In

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Synthesis of New Chiral Monosulfonamides Prepared from (11*R*,12*R*)-11,12-Diamino-9,10-dihydro-9,10-ethanoanthracene and their Use as Ligands for Asymmetric Catalysis

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Abstract. New chiral monosulfonamides **6-16** containing (11*R*,12*R*)-diamino-9,10-dihydro-9,10-ethanoanthracene as carbon skeleton were prepared. Compounds **6-12, 15** and **16** were used as optically active ligands in the enantioselective ethylation of benzaldehyde. Moreover, the monosulfonamides **6-10** were tested in the asymmetric transfer hydrogenation (ATH) of acetophenone with Rh(Cp*)L* complex.

Key words: Monosulfonamide, asymmetric catalysis, enantioselective addition.

Resumen. Nuevas monosulfonamidas quirales **6-16** teniendo a la (11*R*,12*R*)-diamino-9,10-dihidro-9,10-etanoantraceno como esqueleto carbonado fueron preparadas. Los compuestos **6-12**, **15** y **16** se utilizaron como ligantes ópticamente activos en la etilación enantioselectiva de benzaldehído. Además, las monosulfonamidas **6-10** se probaron en la reducción asimétrica por transferencia de hidrógeno (ATH) de acetofenona con Rh(Cp*)L* utilizándolos como catalizadores.

Palabras clave: Monosulfonamida, catálisis asimétrica, adición enantioselectiva.

Introduction

Chiral secondary alcohols are important structures present in natural products and in many pharmaceutical compounds, and are also precursors for many other complex organic molecules [1]. Hence, there is need to develop new methods for making chiral secondary alcohol. Asymmetric catalysis has been a powerful tool to obtain enantiomerically pure or enriched alcohols, mainly by nucleophilic additions to carbonyl compounds [2]. Several and efficient chiral ligands have been used, alone or in the presence of Lewis acids. These include amino alcohols [3-6], α-hydroxy acids [7], α-amino amides [8], α-hydroxy amides [9], and hydroxysulfonamides [10-14].

Our group has recently reported the preparation of bis(sulfonamide) **1**, containing (11*R*,12*R*)-11,12-diamino-9,10-dihydro-9,10-ethanoanthracene as carbon skeleton [15]. The bis(sulfonamide) **1** was used as ligand in the asymmetric alkylation of prochiral ketones with diethyl zinc in high yield and enantioselectivities up to 99% *ee* (Figure 1).

Subsequently, König *et al.* [16] described the synthesis of novel tetradentate sulfonamide ligands and used them in the catalytic asymmetric alkylation of aldehydes with diethylzinc. Quantitative yields of the corresponding secondary alcohol and good asymmetric induction (70% yield and 74% *ee*) were obtained with ligands **2a-b**.

Somanathan *et al.* [17-18] reported the use of monosulfonamide ligand **3a-b**, derived from *trans*-(1*R*,2*R*)-cyclohexane-1,2-diamine, in the asymmetric transfer hydrogenation of aromatic ketones. Enantioselectivities ranged from 70 to 99% and good yields for the synthesis of 1-phenylpropanol derivatives were achieved.

Recently Hirose [19] and co-workers described the synthesis of chiral 1,3-amino sulfonamides, **4, 5**.

They were prepared from (-)-*cis*-2-benzamidocyclohexanecarboxylic acid and studied by tested as ligands for catalytic enantioselective addition of diethyl zinc to aldehydes. They provided secondary alcohols in quantitative yields and in good to excellent enantioselectivities (up to 98% *ee*).

These reports prompted us to prepare the monosulfonamides **6-12, 15** and **16** and to test their catalytic activity. First,

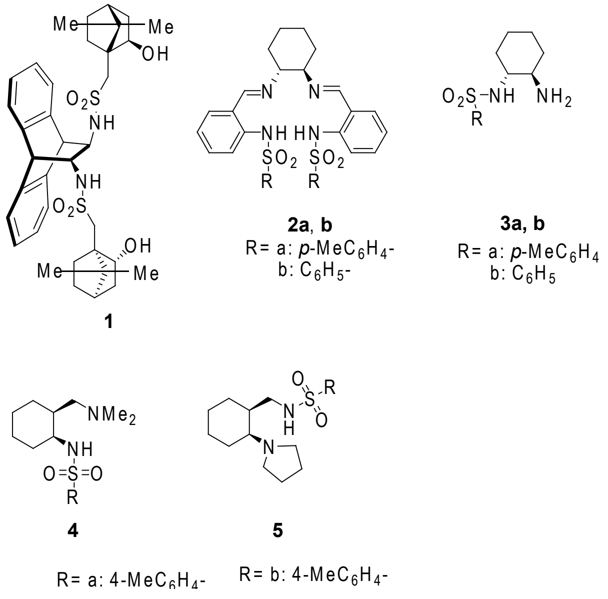

Fig. 1. Chiral sulfonamides used in asymmetric catalysis.

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Oxygen–chlorine interactions in the transition state of asymmetric Michael additions of carbonyl compounds to β-nitrostyrene

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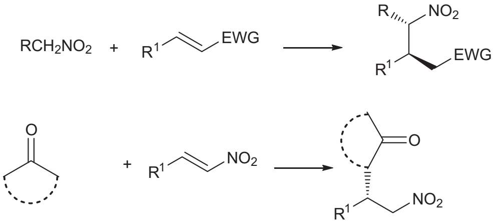
ABSTRACT

An oxygen–chlorine interaction is reported in the transition state of the Michael addition of acetone to nitrostyrene catalyzed by enantioenriched monosulfonamides. The interaction between the oxygen from the nitro group and the chlorine at the *ortho*-position of the sulfonamide moiety is supported by theoretical calculations. Asymmetric Michael addition products catalyzed by monosulfonamides were obtained in moderate yields and enantioselectivities.

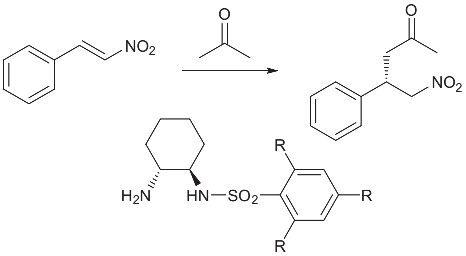
1. Introduction

The catalytic Michael reaction is an important and well-studied process for stereoselective carbon–carbon bond formation in organic synthesis.[1] In recent years, the field of asymmetric organocatalytic Michael reactions has received widespread attention.[2] Among the reactions studied, the conjugate addition of nitroalkanes to α,β-unsaturated systems and additions involving carbonyl compounds to α,β-unsaturated nitroalkenes are of great interest (Scheme 1).[3,4] The products obtained are direct precursors to important structural moieties, such as γ-aminocarbonyls, 2-pyrrolidones, and 2-piperidones.[3a]



Scheme 1. Michael addition of nucleophiles to α,β-unsaturated systems with an electron-withdrawing group.

Various classes of bifunctional organocatalysts have been employed in Michael additions, such as thioureas, cinchona alkaloids, proline derivatives, and sulfonamides.[4a] Having a library of enantioenriched monosulfonamides in hand,[5] we turned our attention to using these ligands as organocatalysts in Michael additions. Herein we report the use of enantioenriched mono-sulfonamides derived from (1*R*,2*R*)-cyclohexanediamine as bifunctional organocatalysts to promote the addition of carbonyl compounds to β-nitrostyrene (Scheme 2).



Scheme 2. Michael addition of acetone to nitrostyrene catalyzed by chiral monosulfonamides.

The sulfonamide organocatalyst acts as a weak hydrogen bond donor, and at the same time contains a basic primary amino group that can activate the nucleophilic reaction partner (in this case, acetone) by generation of an enamine. Thus, the catalyst is proposed to be bifunctional in the transition state of the reaction (Fig. 1A).

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SYNTHESIS AND COMPARATIVE STUDY OF *N*-ISOPROPYLACRYLAMIDE (NIPAAm) HYDROGEL AND *N*-ISOPROPYLACRYLAMIDE-METHYL-METHACRYLATE (NIPAAm-MMA) GEL

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The purpose of this study was to investigate the behavior of the *N*-isopropylacrylamide (NIPAAm) hydrogel and *N*-isopropylacrylamide-methyl-methacrylate (NIPAAm-MMA) gel in a range of temperature close to that of the human body for potential soft tissue repair. The preparation of NIPAAm hydrogel and NIPAAm-MMA gel was done through the free radical polymerization technique. A change in the swelling of the NIPAAm hydrogel as a function of the temperature with the time, was observed, but not in the NIPAAm-MMA gel. The samples were tested at 22 ^{o}C, 29 ^{o}C, 35 ^{o}C, 36 ^{o}C, and 37 ^{o}C, and characterized using FT-IR. Thermal stability of all the samples was studied by means of thermogravimetric analysis and the surface morphology of the NIPAAM hydrogel is compared with that of the copolymer of NIPAAm-MMA gel by atomic force microscopy (AFM).

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Keywords: Hydrogel**;** NIPAAm**;** Free radical polymerization

1. Introduction

Sensitive gels change their volume depending on the properties of the environment they are in, though most are liquid. This volume change is reversible and can be continuous or discontinuous, depending on the chemical structure of the sensitive hydrogel. Tanaka brought these materials to worldwide attention through his pioneering work on the temperature sensitive *N*-Isopropylacrylamide (NIPAAm) polymers and copolymers, and on solvent sensitive acrylamide polymers [1-2]. Hydrogels having nanoside dimensions could have many applications because of their size. As it is well known, many reported hydrogels possess stimuli responsive behavior such as thermo- and pH-sensitivity just as macrogels [3]. Because many recent review papers describe the interest in hydrogels for biomedical applications, we do not aim to give a complete overview here; we only shortly highlight the advantages of hydrogels with a few appealing examples related to potential soft tissue repair and delivery [4-7]. Hydrogels are sub-micron-size water-swollen particles composed of a three-dimensional network of hydrophilic polymer chains linked by

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Synthesis of C_2-symmetric 1,2-diamine-functionalized organocatalysts: mimicking enzymes in enantioselective Michael addition reactions

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ABSTRACT

We report the synthesis of novel chiral wedge shaped C_2-symmetric 1,3-benzenedisulfonamides as organocatalysts that hydrogen bond to the nitroolefins in the transition state of the Michael addition of carbonylic compounds, mimicking natural enzymes, leading to products in excellent yields (up to 99%) and enantioselectivities (up to 99%).

Introduction

The Michael reaction using organocatalysts is one of the most efficient and broadly applicable carbon–carbon bond forming reactions known, because a wide variety of acceptors and donors can be used with high stereoselectivity.[1,2] Designing organocatalysts as small enzyme mimics to catalyze the Michael reaction has been a challenge to synthetic organic chemists over the years. Various classes of bifunctional organocatalysts have been employed in the enantioselective Michael addition, such as thioureas, cinchona alkaloids, proline derivatives and sulfonamides.[3] One of the main objectives of our research group is to design bifunctional organocatalysts that mimic enzymes by dual activation between two functionalities in a reaction involving achiral reactants.

In the search for new multifunctional catalysts that mimic enzymes, we recently reported the synthesis and catalytic activity of a series of halogenated (X = Cl, Br) enantioenriched monosulfonamides as organocatalysts (Scheme 1). [4] These catalysts exhibited novel Cl···O bonding interactions (Fig. 1), in addition to the expected hydrogen bonding in the transition state of conjugate Michael addition of carbonyls to nitrostyrene.[4] This remarkable trifunctional interaction involving enamine formation, Cl···O_{nitro} interaction, and H–O_{nitro} bonding in the transition state was found computationally to provide structural rigidity, enhancing the yields of the Michael addition product.

Based on the hypothesis that multifunctional enantioselective catalysts would exhibit greater enantioselectivity, we decided to explore, C_2-symmetric organocatalysts. C_2 and C_3-symmetric catalysts have been efficiently used as organocatalysts in the asymmetric Michael addition reactions; these ligands offer two or three activation sites and may mimic an enzymatic catalysts.[5] An apparent advantage of C_2-symmetric catalysts is that they reduce the number of diastereomeric transition states, simplifying the analysis of the stereochemical outcome. Based on these considerations, we synthesized a series of C_2-symmetric bis-sulfonamide ligands derived from 1,3-benzene sulfonyl chloride and biphenyl-4,4′-disulfonyl chloride and tested them in the asymmetric transfer hydrogenation of aromatic ketones (ATH) with Ru(II) and Rh(III) complexes (enantioselectivities up to 99%, yields up to 99%).[6] Interestingly, the structural features of these C_2-symmetric bis-sulfonamide ligands are also suitable as organocatalysts for the conjugate Michael addition reaction; with a primary amine group that can activate acetone by formation of an enamine intermediate, and a proton donor from the sulfonamide group ($NH\text{-}SO_2Ar$) for hydrogen bonding to the nitro group of the alkene. Furthermore, previous literature showed acetate anion recognition by similar bis-1,3-benzenedisulfonamides, where the two acetate oxygens

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Research Article

A Novel and Highly Regioselective Synthesis of New Carbamoylcarboxylic Acids from Dianhydrides

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A regioselective synthesis has been developed for the preparation of a series of N,N'-disubstituted 4,4′-carbonylbis(carbamoylbenzoic) acids and N,N'-disubstituted bis(carbamoyl) terephthalic acids by treatment of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (**1**) and 1,2,4,5-benzenetetracarboxylic dianhydride (**2**) with arylalkyl primary amines (**A**-**N**). The carbamoylcarboxylic acid derivatives were synthesized with good yield and high purity. The specific reaction conditions were established to obtain carbamoyl and carboxylic acid functionalities over the thermodynamically most favored imide group. Products derived from both anhydrides **1** and **2** were isolated as pure regioisomeric compounds under innovative experimental conditions. The chemo- and regioselectivity of products derived from dianhydrides were determined by NMR spectroscopy and confirmed by density functional theory (DFT). All products were characterized by NMR, FTIR, and MS.

1. Introduction

Some N-aryl 2-carbamoylbenzoic acids, commonly known as phthalamic acids, are auxin transport inhibitors in plants [1–4]. The activity of these phytotropins is directly related to the carboxylic acid group attached to an aromatic ring in the ortho position of a second aromatic ring through a conjugated or a planar system of atoms. The spatial requirement for a high activity is the specific distance between the two aromatic ring centers (7.3 Å). Other biological effects of this molecule in plants include the ability to inhibit the polar transport of auxins, to abolish the apical dominance effect, and to prevent the geo- and phototropic response. In particular the N-1-naphthyl-2-carbamoylbenzoic acid (NACBA) is known as a potent inhibitor of auxins transport and geotropic curvature. It also has the capacity to bind to fractions containing plasma membrane vesicles from maize coleoptiles.

Recently, the synthesis of N-aryl-2-carbamoylbenzoic acids under microwave assisted conditions from phthalic anhydride and aryl or heterocyclic amines in the absence of solvent with yields 51–99% has been reported [5]. Significant research findings show that these N-arylphthalamic acids induce hyperlipidemia in Swiss white mice and also an increase in body weight of the animals, in contrast with the hypolipidemic activity showed by their phthalimide analogues [6].

In addition, 2-carbamoylbenzoic acids and structurally related compounds have shown attractive pharmaceutical and agricultural applications as novel anti-inflammatory, immunomodulatory, antiproliferatory, antithrombotic, and

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Article

Antibacterial Activity of New Oxazolidin-2-One Analogues in Methicillin-Resistant *Staphylococcus aureus* Strains

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Abstract: *Staphylococcus aureus* is one of the most common causes of nosocomial infections. The purpose of this study was the synthesis and *in vitro* evaluation of antimicrobial activity of 10 new 3-oxazolidin-2-one analogues on 12 methicillin resistant *S. aureus* (MRSA) clinical isolates. *S. aureus* confirmation was achieved via catalase and coagulase test. Molecular characterization of MRSA was performed by amplification of the *mecA* gene. Antimicrobial susceptibility was evaluated via the Kirby-Bauer disc diffusion susceptibility test protocol, using commonly applied antibiotics and the oxazolidinone analogues. Only (*R*)-5-((*S*)-1-dibenzylaminoethyl)-1,3-oxazolidin-2-one (**7a**) exhibited antibacterial activity at 6.6 µg. These results, allow us to infer that molecules such as **7a** can be potentially used to treat infections caused by MRSA strains.

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Research Article

Improving the Efficiency of a Coagulation-Flocculation Wastewater Treatment of the Semiconductor Industry through Zeta Potential Measurements

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Efficiency of coagulation-flocculation process used for semiconductor wastewater treatment was improved by selecting suitable conditions (pH, polyelectrolyte type, and concentration) through zeta potential measurements. Under this scenario the zeta potential, ζ, is the right parameter that allows studying and predicting the interactions at the molecular level between the contaminants in the wastewater and polyelectrolytes used for coagulation-flocculation. Additionally, this parameter is a key factor for assessing the efficiency of coagulation-flocculation processes based on the optimum dosages and windows for polyelectrolytes coagulation-flocculation effectiveness. In this paper, strategic pH variations allowed the prediction of the dosage of polyelectrolyte on wastewater from real electroplating baths, including the isoelectric point (IEP) of the dispersions of water and commercial polyelectrolytes used in typical semiconductor industries. The results showed that there is a difference between polyelectrolyte demand required for the removal of suspended solids, turbidity, and organic matter from wastewater (23.4 mg/L and 67 mg/L, resp.). It was also concluded that the dose of polyelectrolytes and coagulation-flocculation window to achieve compliance with national and international regulations as EPA in USA and SEMARNAT in Mexico is influenced by the physicochemical characteristics of the dispersions and treatment conditions (pH and polyelectrolyte dosing strategy).

1. Introduction

In the industrial wastewater treatment of semiconductors, the most appreciated characteristic of polyelectrolytes (PE) is their solid-liquid separation efficiency, with extensive application in purification of drinking water, industrial raw and process water, municipal sewage treatment, mineral processing and metallurgy, oil drilling and recovery, paper and board production, and so forth [1–9]. Polyelectrolytes can be used alone or in association with other flocculant aids, such as inorganics salts, surfactants, or even as a second polymer. Compared with inorganic coagulants, there are some advantages by using organic polyelectrolytes [1, 6, 7, 10, 11]: lower dose requirements, a smaller volume of sludge, a smaller increase in the ionic load of the treated water, and cost savings up to 25–30%.

It is well known that the efficiency of a certain polyelectrolytes in flocculation processes is evaluated as a function of four main parameters: the optimum flocculant concentration, which should be as low as possible; isoelectric point (IEP) that determines the effective pH range; and the flocculation window, which must be as large as possible [12]. To improve the solid/liquid separation process, polymeric flocculants, mainly polycations, have been used [1, 6–9]. The main

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Coagulation–flocculation mechanisms in wastewater treatment plants through zeta potential measurements

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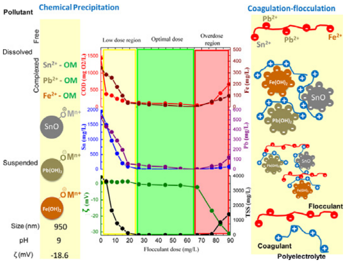
HIGHLIGHTS

- A well planned polyelectrolyte dosing strategy plays a crucial role in successful coagulation–flocculation process.
- pZ–pH plots are a powerful tool to plan polyelectrolytes dosage and to discover coagulation–flocculation mechanisms.
- Previously prepared polyelectrolytes dispersions improved resulting water quality after a coagulation–flocculation process.

GRAPHICAL ABSTRACT



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ABSTRACT

Based on the polyelectrolyte-contaminant physical and chemical interactions at the molecular level, this article analyzed and discussed the coagulation–flocculation and chemical precipitation processes in order to improve their efficiency. Bench experiments indicate that water pH, polyelectrolyte (PE) dosing strategy and cationic polyelectrolyte addition are key parameters for the stability of metal–PE complexes. The coagulation–flocculation mechanism is proposed based on zeta potential (ζ) measurement as the criteria to define the electrostatic interaction between pollutants and coagulant–flocculant agents. Polyelectrolyte and wastewater dispersions are exposed to an electrophoretic effect to determine ζ. Finally, zeta potential values are compared at pH 9, suggesting the optimum coagulant dose at 162 mg/L polydadmac and 67 mg/L of flocculant, since a complete removal of TSS and turbidity is achieved. Based on the concentration of heavy metals (0.931 mg/L Sn, 0.7 mg/L Fe and 0.63 mg/L Pb), treated water met the Mexican maximum permissible limits. In addition, the treated water has 45 mg O_2/L chemical oxygen demand (COD) and 45 mg C/L total organic carbon (TOC). The coagulation–flocculation mechanism is proposed taking into account both: zeta potential (ζ)–pH measurement and chemical affinity, as the criteria to define the electrostatic and chemical interaction between pollutants and polyelectrolytes.

1. Introduction

The electroplating wastewater, in the semiconductor industry, contains dissolved and suspended heavy metals (such as Sn, Cr, Ni, Pb, and Cu, among others), making necessary to find a suitable

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SYNTHESIS OF 1*H*-BENZOXAZINE-2,4-DIONES FROM HETEROCYCLIC ANHYDRIDES: EVALUATION OF ANTIOXIDANT AND ANTIMICROBIAL ACTIVITIES

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A facile one-step synthesis of 1*H*-benzoxazine-2,4-diones from heterocyclic anhydrides and TMSA was described. This paper determines their antimicrobial activity against nine human bacterial pathogens by the broth microdilution method; antioxidant activity by DPPH• inactivation and a ferric-reducing power assay; and toxicity by a brine shrimp, *Artemia salina,* assay. The 1*H*-benzoxazine-2,4-dione yields were in the range of 57 to 98%. The novel compound 1*H*-pyrazino[2,3-][1,3]oxazine-2,4-dione **4c** showed the highest antioxidant capacity (DPPH 35.4% and FRAP 0.063 µmol TEs/µmol).

Keywords: 1*H*-benzoxazine-2,4-dione; antimicrobial activity; antioxidant activity; toxicity.

INTRODUCTION

Currently, microbial resistance to first-line antibiotic agents is a public health concern, and new drugs are required to treat infected patients. Several heterocyclic structures have shown antibacterial activity, including benzoxazine-2,4-diones.[1] Benzoxazine-2,4-diones are potential pharmacophores because of their registered activities: potent inhibitor of hepatitis C virus,[2] butyrylcholinesterase inhibitor,[3] antiallergic,[4] antitumor,[5] antipsychotic,[6] antileishmanial,[7] and antimycobacterial,[8] among others. The syntheses of benzoxazine-2,4--diones from anthranilic acid derivatives,[9] isatin,[10] allenamides,[11] and carbamoylbenzoic acid[12] have been reported. Rao *et al.*[13] reported the synthesis of isatoic anhydride from phthalimide and sodium hypochlorite in a basic one-pot solution. This is the only methodology used to produce isatoic anhydride on a large scale. However, if the temperature is not controlled during the course of the reaction, the yield is significantly reduced. In addition, large effluents of wastewater are produced. In general, these processes involve several reaction steps and employ expensive, noncommercial, or dangerous reagents; thus, a better process must be designed.

Viewing the process from a different perspective, there is an increasing interest in compounds with high antioxidant activities, which could counteract the oxidative stress associated with diseases.[14] Antioxidant activity screening is commonly done by *in vitro* assays, as in the ABTS$^{\bullet+}$,[15] ferric-reducing,[16,17] and DPPH[18,19] methods.

Recently, we have reported the synthesis of heterocyclic compounds[20-24] with antiparasitary[25] and antioxidant[26,27] activities. In the following sections, an easy one-step synthesis of 1*H*-benzoxazine-2,4-diones from heterocyclic anhydride with TMSA is presented, and their toxicity, antimicrobial activities, and antioxidant activities are reported.

EXPERIMENTAL

Chemistry

All reagents were purchased in the highest quality available and were used without further purification. The solvents used in column chromatography were obtained from commercial suppliers and used without distillation. Nuclear Magnetic Resonance of ^{1}H (200 MHz) and ^{13}C (50 MHz) spectra were recorded on a Varian Mercury 200 MHz Spectrometer in DMSO-d_6 with TMS as an internal standard. Chemical ionization mass spectra were obtained with a Varian Titan 4000 ion trap GC-MS, and the intensities were reported as a percentage relative to the base peak after the corresponding *m/z* value. HR-MS was recorded on an ESI/APCI-TOF Bruker model MicroTOF-II-FocusTM at the Universidad Autónoma Metropolitana, Campus Iztapalapa. Infrared spectra were recorded on a Cary 660 series FTIR-ATR spectrophotometer. Melting points were obtained on a Stuart apparatus model SMP30; the reported value is the average of three separate experiments.

General procedure for the synthesis of benzoxazine-2,4-diones

The heterocyclic anhydride in THF (1.0 mM) and trimethylsylilazide (TMSA, 1.05 equiv.) were stirred in a Schlenk bulb for 17 h at 53 ºC, then temperature was increased to reflux and maintained for 2 h. The resulting solution was concentrated under vacuum pressure until a solid was formed. The solid was washed with diethyl ether (5 x 4 mL) to obtain 1*H*-benzoxazine-2,4-diones in high purity.

1*H*-3,1-benzoxazine-2,4-quinone (**4a**). (For full characterization see lit.);[28,29] CAS number: 118-48-9; yield 85%; white solid; R_f 0.58 (petroleum ether/EtOAc 1:1 v/v); ^{1}H-NMR (200 MHz, DMSO-d_6): δ 11.74 (br s, 1H), 7.91 (dd, J_1=8.07, J_2=1.1 Hz, 1H), 7.74 (td, J_1=7.79, J_2=1.28 Hz, 1H), 7.25 (m, 2H); ^{13}C-NMR (50 MHz, DMSO-d_6): δ 159.9, 147.1, 141.4, 136.9, 128.9, 123.5, 115.3; CG-MS *m/z*: 164 [M+H]$^+$

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Research Article

A Novel One-Pot and One-Step Microwave-Assisted Cyclization-Methylation Reaction of Amino Alcohols and Acetylated Derivatives with Dimethyl Carbonate and TBAC

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A simple and efficient microwave-assisted methodology for the synthesis of 4-substituted-3-methyl-1,3-oxazolidin-2-ones from amino alcohols catalyzed by a ionic liquid was developed. This novel one-pot and one-step cyclization-methylation reaction represents an easier and faster method than any other reported protocols that can be used to obtain the desired products in good yields and high purity. Applying microwave irradiation at 130°C in the presence of TBAC, dimethyl carbonate acts simultaneously as carbonylating and methylating agent and surprisingly promotes an *in situ* basic trans esterification when a N-acetylated amino alcohol is used as starting material. Furthermore, dimethyl carbonate worked better than diethyl carbonate in performing this reaction.

1. Introduction

In general, amino alcohols are readily available by reduction of an α-aminoacid and are important precursors in the synthesis of 1,3-oxazolidin-2-ones [1–6]. Phenylalanine-derived aminoalcohols, phenylglycine, and valine, among others, are used for the preparation of commercially important 1,3-oxazolidin-2-one chiral auxiliaries. In this context, a large number of reagents have been used in the presence of amino alcohols to synthesize 1,3-oxazolidin-2-ones. Early methods are focused to employ phosgene in reactions with amino alcohols [7–9]. Other early efforts toward the synthesis of 1,3-oxazolidin-2-ones consist in the fusion of urea with the amino alcohols above their melting points [10–12]. Cyclization with tosyl chloride can be achieved with N-methylated Boc amino alcohol derivatives [13]. More recently, with the decreasing use of phosgene, an efficient synthesis of 1,3-oxazolidin-2-ones from diethyl carbonate (DEC) has become prevalent [3, 14, 15].

In general, the preparation of 4-substituted-N-alkyloxazolidin-2-ones is achieved through a two steps sequence, that is, the carbonylation of 1,2-amino alcohols or N-acetylated amino alcohols with phosgene or triphosgene, followed by the N-alkylation of the resulting 1,3-oxazolidin-2-one with an alkyl halide (R^2X) or a basic deacetylation and alkylation (Scheme 1).

These procedures are not ecofriendly due to risks associated with toxic and corrosive reagents, such as phosgene and carcinogenic alkyl halides. A safer, easier, and ecofriendly alternative can be conceived with the use of nontoxic dimethyl carbonate (DMC). There are only a few examples where dimethyl carbonate simultaneously acts as carbonylating and alkylating agent. Among them, the case of oximes with an α–CH_2 group for the synthesis of 3-methyl-4,5-disubstituted-4-oxazolin-2-ones [16]. More recently, the preparation of N-methylbenzoxazol-2-ones from o-aminophenol and dimethyl carbonate with catalytic

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Research Article

Synthesis and Antioxidant Evaluation of Enantiomerically Pure Bis-(1,2,3-triazolylmethyl)amino Esters from Modified α-Amino Acids

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The efforts for synthesis of enantiomerically pure bis-(1,2,3-triazolylmethyl)amino esters **6** are reported in good yields from an *in situ* generated α-azidomethyl ketone. Optimum experimental conditions were established for preparation of α-halomethyl ketones **10** and α-*N,N*-dipropargylamino esters **11**, all derived from α-amino acids. The starting materials reacted under conventional click chemistry conditions, revealing a specific reactivity of bromomethyl ketones over chloromethyl ketones. The antioxidant activity of compounds **6** was assayed by DPPH method. The compound **6c** with an IC_{50} of $75.57 \pm 1.74\ \mu g\ mL^{-1}$ was the most active. Technically, this methodology allows the preparation of a combinatorial library of analogues with different structural characteristics depending on the nature of the modified α-amino acids employed in the synthesis.

1. Introduction

Click chemistry has been defined as an efficient and an almost perfect method (very selective, with high yields and wide scope) for the synthesis of new and diverse compounds based in a carbon-heteroatom bond formation. This reaction has been particularly useful for coupling two molecules, azides and alkynes, to get 1,2,3-triazole compounds [1]. However, it was only after the discovery of copper catalysis that its applications began to be studied [2]. Click chemistry meets the requirements of an innovative functionalization strategy for biomolecules because it is efficient, selective, and without side reactions. Rostovtsev et al. [3] and Tornøe et al. [4] have reported that 1,4-disubstituted 1,2,3-triazoles are specifically prepared from azides and terminal alkynes under copper(I) catalysis to give 1,4-substituted products with high regioselectivity. The regioisomeric 1,5-disubstituted triazoles are available from azides and terminal alkynes by the use of either magnesium acetylides or ruthenium catalysts [1, 5, 6]. 1,2,3-Triazole compounds have attracted attention because they exhibit a broad variety of biological activities. For example, compounds such as **1** are active against *Mycobacterium tuberculosis* [7]; other compounds act as anticancer **2** [8], antifungal **3** [9], or antitumor agents **4** [10], Scheme 1. Some biomedical applications have been described, for example, the labelling of biomolecules [11]. In addition, 1,2,3-triazoles have been used in the coupling of modified α-amino acids in oligopeptide synthesis [4, 12–17]. Furthermore, this class of modified oligopeptides **5** showed activity as inhibitors of cysteine protease CPB2.8ΔCTE in *Leishmania mexicana* [18] and antiviral activity against HIV-1 gp120 [19, 20].

The cycloaddition of azides and alkynes is typically carried out in refluxing toluene, but labile molecules may not be stable under these conditions. Also, although organic azides are generally safe compounds, those of low molecular weight can be unstable and, therefore, difficult to handle. This is especially true for small molecules with several azide functionalities, which would be of much interest for the generation of polymeric structures. Thus, a methodology that avoids isolation of organic azides as intermediates is

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Size-Dependent Enhanced Energy Transfer from Tryptophan to CdSe/Mercaptopropionic Acid Quantum Dots: A New Fluorescence Resonance Energy Transfer Nanosensor

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ABSTRACT

We report here the interaction of mercaptopropionic acid (MPA)-capped CdSe quantum dots (QDs) of different sizes with tryptophan in aqueous solution. Two populations of QDs emitting at 578 and 596 nm were tested in two concentration ranges. CdSe/MPA QDs efficiently quenched the photoluminescence (PL) of tryptophan in a size-dependent manner. The results revealed that the binding constant (K_A) and the number of binding sites (n) were higher for larger QDs, and the values of $\log K_A$ were proportional to n. The PL of QDs was gradually enhanced with increasing amount of tryptophan, indicating a fluorescence resonance energy transfer (FRET) from tryptophan to QDs. The Förster radius and donor–acceptor distances were estimated from the experimental measurements of energy transfer efficiency. A more effective process occurred in the larger-sized QD acceptors. Under the optimized conditions, QDs596 showed a linear increase of PL in the presence of tryptophan in the concentration range of 0 to 9×10^{-7} M ($R = 0.995$) and a detection limit of 5.4×10^{-7} M. No interference from coexisting amino acids such as tyrosine, phenylalanine and glycine was found. High selectivity and sensitivity and a fast response time make CdSe/MPA QDs a suitable nanosensor for the quantitative determination of tryptophan.

KEYWORDS: CdSe QDs, Nanoparticle Size, Energy Transfer, Tryptophan Detection.

ARTICLE

1. INTRODUCTION

Quantum dots (QDs) have attracted considerable attention in recent years for their applications in chemistry, physics and biology.[1] As a result of quantum confinement, such nanoparticles have optical and electronic properties that can be adjustable through their size.[2] Compared to conventional organic fluorophores, QDs have narrow and symmetric emission bands and high photochemical stability.[3,4] The modification of QDs with biomolecules has been widely used in biological field for various applications such as cell and tissue labeling,[5] for bioimaging[6] and drug delivery.[7] In contrast to the large number of reports on the use of QDs as fluorescent labeling for biomolecules, the applications of QDs as a new class of nanomaterials in chemical sensing are still in the early stages. Some studies based on the chemical sensing of small molecules and ions using QDs have been reported.[8–14]

Förster resonance energy transfer (FRET) is a process whereby a donor (D) transfers energy to an acceptor (A) via a through-space-dipole–dipole interaction. FRET occurs over distances of 1–10 nm, when there is appreciable overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor. Analytical methods based on FRET have high sensitivity, and are very easy to perform. FRET-based methods are very useful in detecting ligand-receptor binding by measuring the enhancement in fluorescence intensity of the acceptor. QDs have been used in FRET systems, both as donors[15–19] and as well as energy acceptors.[20–24]

Amino acids are biomolecules of great relevance as they involve in several functions in the living organism. Tryptophan is one of the most important amino acids for human nutrition, and is also involved in neurotransmission processes as a serotonin and melatonin precursor.[26,27] As the distribution, transport and toxicity of QD are closely

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New dual emission fluorescent sensor for pH and Pb(II) based on bis(napfthalimide) derivative

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This paper describes a novel dual emission bis-1,8-naphthalimide sensor for selective determination of pH and Pb^{2+} ions. The influence of the variability in the backbone that links the two fluorophores (naphthalimides) as a function of pH and metal ions was studied by UV–visible and fluorescence spectroscopy. Compounds **1**(**a–d**) with different length alkyl linkers $(CH_2)_n$ ($n=1$, 2, 4 and 6) showed no excimer formation in aqueous solution. Fluorescence emission of these derivatives varied in a narrow range of pH (5–8) and was only slightly influenced by the addition of metal ions in CH_3CN solutions. However, derivative **1e** with amino-containing spacer (CH_2–NH–CH_2) showed excimer emission in aqueous solution, a wide response to pH (2.5–9.5) and fluorescence enhancement with selective behavior towards metal ions. The pH sensor based in derivative **1e** has a sufficient selectivity for practical pH monitoring in the presence of Li^+, Na^+, K^+, Cs^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+}. The coordination chemistry of these complexes was studied by UV–Vis, fluorescence and ^{1}H NMR. This chemosensor displayed high selectivity fluorescence enhancement toward Pb^{2+} ions in the presence of the metals ions mentioned in CH_3CN solutions. Competitive assays show that a 1-fold of metal cations in each case, compared with Pb^{2+} ions, results in less than $\pm 5\%$ fluorescence intensity changes. Linear calibration up to 1×10^{-5} M for Pb(II) ions ($R=0.9968$) was obtained and detection limit resulted of 5.0×10^{-8} M.

1. Introduction

The determination of pH has a great interest in different areas such as environmental monitoring, clinical analysis, control and monitoring of biochemical reactions, industrial processes, development of new pharmaceutical products and scientific researches [1–7]. Although the measurement of pH based on electrochemical method is well established and known, it has disadvantages and limitations, for example, the signal can be influenced by electromagnetic fields and aggressive analytes (alkaline solutions or F^- ions), which can destroy the glass surface of the electrode. The pH sensors based in optical measurements offer very promising alternatives that eliminate these drawbacks. They are versatile, easy to miniaturize, inexpensive and can be used for remote sensing. In particular, the fluorescence method is sensitive, selective and provides the possibility of fluorescence imaging measurement.

On the other hand, heavy metals represent an environmental concern due to their harmful effects on human health. In particular, lead produces a wide variety of health effects such as mental retardation, cardiac and neurologic diseases, even when present in low concentration. The determination of lead by analytical methods such as flame or plasma techniques can lead to a low precision and sensitivity due to the effects of high back-ground and chemical interferences. Thus, the fluorimetric methods are an alternative that can provide good selectivity, sensitivity and low cost. Despite these advantages, most fluorimetric methods for determination of heavy metals are based on a fluorescence quenching, which is not the best alternative, so there is a great interest in developing fluorescent sensor that give rises an increase in the analytical signal.

The measurement of fluorescence can be affected by fluctuations in excitation source, photobleaching of the fluorophore reagent, detector drifts and background fluorescence. These effects can be avoided using ratiometric measurements [8–11]. The method is based on fluorescence intensity measurement of a sensitive indicator at two different wavelengths that prevents most of the systematic errors associated with this type of measurement. The number of special fluorophores sensitive to pH or metal ions with dual excitation or emission wavelengths is limited. An approach for

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Evaluation of the Physicochemical Behavior of Waste Water Treatment Polyelectrolytes with Metal Ions

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ABSTRACT

In this paper is describing the physicochemical behavior of polyelectrolytes (PEs) used in waste water treatment with mono-, di- and trivalent metal ions as K^+, Mg^{2+}, Zn^{2+}, Fe^{3+}, Sn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+} and Cr^{3+}. A coagulant polyelectrolyte Poly(vinyl sulfate) potassium salt (PVSK), and a commercial available Flocculant Trident 2756, were used as models for the study. The colloidal titration UV-Vis spectroscopy technique was successfully implemented in order to evaluate the complexation of PEs with Toluidine Blue O (OTB) and the ability of different metal ions to displace the OTB from the PE-OTB complex and form the PE-metal ion complex. From the experiments was concluded that PVSK has a high affinity for Al^{3+} and Mg^{2+} while the Flocculant has the highest affinity for Sn^{2+} followed by Zn^{2+} and Mg^{2+}. The absorbance profiles of polyelectrolyte-OTB complex (Absorbance vs. Metal/PE) were used to calculate association constants. On the other hand, the mass balance of OTB and its absorbance profiles were used to calculate the association constants of polyelectrolyte-metal ion complexes. Thus metal ions with the highest affinities have the highest association constant. Metal ions with the highest affinities present the highest values of association constant.

Keywords: Polyelectrolytes; Metal Ions; Colloidal Titration; UV-Vis Spectroscopy; O-Toluidine; Wastewater Treatment

1. Introduction

Polyelectrolyte chains have atoms or groups of atoms which have the ability to chelate or exchange sities with metal ions [1]. The most common coordinating atoms present in a polymer chain, either central or side chain, are nitrogen, oxygen, phosphorus and sulfur [2]. For those polymers in which the polymer-metal ion interaction involves an ion exchange process, the most common are the quaternary ammonium with chloride, sulphate and hydroxyl counterions [3]. Polyelectrolyte-metal ion interaction could be electrostatic or may include the formation of coordinated bonds. The type of interaction depends on the chemical nature (ionization potential and electronic affinity) of the functional groups. The variables that affect the PE-metal ion interaction are classified into two groups: intrinsic and extrinsic to the polymer [4]. The former group includes the polymer structure in terms of composition and geometry, which affects the flexibility of the chains in solution: branches of the chain, chemical nature of the functional groups, and their distribution at the polymer chain, etc. The second group includes the charge and type of the metal ion, pH, ionic strength, temperature and dielectric constant of the medium [5,6]. The knowledge of association phenomena of metal ions with charged macromolecules is essential for understanding of their physicochemical behavior in environmental, biological systems and in waste water treatment by coagulation-flocculation [7-9].

Polyelectrolytes are used in coagulation-flocculation processes mainly to remove suspended particles, turbidity and color. However, due to their chemical nature, polyelectrolytes also interact with oppositely charged species as metal ions that are present in the wastewater. For example, the treatment of waste water from semiconductor fabrication industry with high suspended solids content of heavy metals, where the objective is to remove suspended solids as well as heavy metals content. Therefore, it is important to study the physicochemical behavior of polyelectrolytes with different metal ions present in the waste water, with the aim of determining the affinity and capacity of removal of each metal with polyelectrolytes, in order to determinated the optimal

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Article

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Adsorption of Phenol and Chlorophenol Mixtures on Silicalite-1 Determined by GC-MS Method

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Abstract. A method is presented in which gas chromatography coupled with mass spectrometry (GC-MS) allows quantitative simultaneous detection of mixtures of phenol (Ph), 2-chlorophenol (2-CPh), 3-cholorphenol (3-CPh), and 4-cholorophenol (4-CPh) in aqueous mixtures after being adsorbed on silicalita-1, utilizing selected-ion monitoring (SIM) and full-scan modes mass selective detection. GC-MS with SIM at m/z = 64 and m/z = 128 showed good detection selectivity for mixtures of Ph, 2-CPh and 3-CPh (M_1), and 2-CPh and 4-CPh (M_2). Silicalita-1 was obtained from an amorphous organo-alumino-silicic gel from rice husk, an abundant and low cost agricultural waste residue that is readily available in large quantities. This product was used as a sorbent for solid phase extraction of organic analytes from aqueous solutions. The adsorption of the three chlorophenol isomers, *ortho*-, *meta*-, and *para*-, by silicalite-1 has been studied independently, showing that *meta*- and *para*-chlorophenol isomers are adsorbed more than ortho-chlorophenol. However the adsorption behavior of mixtures of these isomers was not reported. In this work, it was found that when the *ortho*-isomer is mixed either with *meta*- or *para*-chlorophenol, considerable differences were observed in the adsorption process; in the studied mixture, the *ortho*-isomer was adsorbed more than the *meta*-and *para*-chlorophenol.

Key words: Silicalite-1, rice husk, GC-MS, *ortho*-chlorophenol, *meta*-chlorophenol, *para*-chlorophenol.

Resumen. En este trabajo se presenta un método cromatográfico acoplado a la espectrometría de masas (GC-MS) que permite la detección simultánea de fenol(Ph), 2-clorofenol (2-CPh), 3-clorofenol (3-CPh), y 4-clorofenol (4-CPh) en mezclas acuosas después de ser adsorbidas sobre silicalita-1, utilizando iones previamente seleccionados (SIM) y el espectro completo de iones. Los iones en SIM de m/z = 64 y 128 mostraron una buena detección y selectividad para mezclas de Ph, 2-CPh, y 3CPh (M_1) y 2-CPh y 4-Cph (M_2). La silicalita-1 se obtuvo a partir de un gel órgano-alumino-silícico amorfo proveniente de cáscara de arroz, material abundante y de bajo costo dado que proviene de residuos agrícolas disponible fácilmente en grandes cantidades. Este producto se utilizó como un sorbente en la extracción en fase sólida de analitos orgánicos a partir de soluciones acuosas. La adsorción de los tres isómeros de clorofenol, *orto, meta,* y *para*, por la silicalita-1 ha sido estudiada de forma independiente, mostrando que los isómeros *meta* y *para* clorofenol se adsorben más que el *orto*-clorofenol. Sin embargo, el comportamiento de adsorción de mezclas de estos isómeros no se ha reportado. En este trabajo, se ha encontrado que cuando el isómero *orto* se encuentra en mezcla con el *meta* o *para*-clorofenol presentan diferencias considerables, como se observó en el proceso de adsorción; en la mezcla estudiada el isómero orto se adsorbe más que el *meta* y *para*-clorofenol.

Palabras clave*:* Silicalita-1, cáscara de arroz, CG-EM, *orto*-clorofenol, *meta*-clorofenol, *para*-clorofenol.

Introduction

Phenols and related compounds are toxic to humans and aquatic life. Chlorophenols are formed as metabolites of agricultural pesticides, in pulp bleaching processes, and as byproducts of the chlorination of drinking waters (NMx-AA-050-1981) [1]. The adsorption technique is one of the alternative treatment processes currently being considered to achieve required levels in the removal of phenols. The adsorption of phenols by different adsorbents has been investigated to identify the relationship between adsorption capacity and adsorbent characteristics such as surface area and pore size distribution for separation applications in the drinking water concentration range [2].

Activated carbon, as one of the active adsorbents, has been extensively used in the process due to its predominant proportion of micropores. Alternative adsorbents studied include naturally occurring materials such as biosorbentes [6], clays, zeolites, and resins [7].

Silicalite-1 (SLC-1), which has a similar structure to ZSM-5, is a molecular sieve that was first synthesized in early 1970s [8]. It was obtained from rice husk through a calcinations process under specific conditions that allow retention of organic matter [9, 10]. This material is a zeolite with a high content of silica [11, 12]. SLC-1 is hydrophobic and can remove organic molecules in liquid or gaseous samples. It is a polymorph of silica with an unusual crystal structure. It has a tetrahedral geometry of mostly 5-membered rings of silicon-oxygen tetrahedra. This spatial distribution has interesting channels with a diameter of 6 Å that are defined by rings of 10 oxygen atoms [8].

The high hydrophobicity of SLC-1 allows it to capture aromatic components of highly toxic simple structures, among

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Selective Reduction of Phenylacetylene with AlMgO Particles used as an Alternative Water-Reactive Generator of Hydrogen

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Abstract A new inorganic material was used to produce hydrogen in situ by contact with water for reduction of unsaturated hydrocarbons. Phenylacetylene reduction into styrene and ethylbenzene was chosen as a model reduction reaction. We show that a fine control over the reaction yield and selectivity can be obtained by controlling the hydrogen release and such parameters of the synthesis as the temperature, water content and the speed of stirring. We found that the largest amount of water at 80 °C and vigorous stirring result in the highest yield and selectivity of the reaction. An alternative way of reaction control is suggested as compared to a conventional way of a catalyst inhibition. The new possibility of the reaction control may be of a wide interest for the laboratory synthesis for a good number of hydrogenation reactions.

Keywords Hydrogenation · AlMgO particles · Hydrogen source · Phenylacetylene

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1 Introduction

The hydrogenation (reduction) of unsaturated organic compounds is a widely used chemical reaction for many industrial applications in such as petro-, food and health industry. The hydrogenation of alkynes is an important industrial process to obtain alkenes and alkanes. The interest in reduction of phenylacetylene (PA) has its origin in the reaction products styrene (ST) and ethylbenzene (EB). Styrene is an extremely important monomer in numerous polymerization reactions, therefore, its production from phenylacetylene is important both from scientific and industrial standpoints. However, the styrene production is not a trivial task, since the hydrogenation reaction (Eq. 1) usually does not stop on the first stage and results in a mixture of styrene with ethylbenzene or even proceeds completely to ethylbenzene alone.

$$\mathrm{Ph{-}{-}C{\equiv}CH \rightarrow Ph{-}{-}C{=}CH_2 \rightarrow Ph{-}{-}CH_2CH_3} \qquad (1)$$

To obtain styrene as a main product the reaction must be thoroughly controlled by tuning the reaction conditions. Therefore, PA partial reduction is a convenient model to evaluate the process design, performance of catalyst or to optimize reaction conditions. There are two main conditions to be fulfilled in any typical hydrogenation reaction: (i) the presence of a catalyst (usually platinum group metals) and (ii) the hydrogen source. Also, there are at least two ways to carry out the hydrogenation: first, hydrogen may be added to the reaction in a gaseous form as a batch (from a balloon under atmospheric pressure or a built hydrogen source under high pressure and/or temperature) or a dilute steam of reactant mixed with hydrogen is made to flow above or through the catalyst (flow hydrogenation) [1]. Thus, there are mainly two ways to gain control over the process rate—by decreasing the