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Probing the cosmic distance duality relation using time delay lenses

Akshay Rana,[a,1] **Deepak Jain,**[b] **Shobhit Mahajan,**[a] **Amitabha Mukherjee**[a] **and R.F.L. Holanda**[c,d,e]

[a]Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India
[b]Deen Dayal Upadhyaya College, University of Delhi, Sector-3, Dwarka, New Delhi 110078, India
[c]Departamento de Física, Universidade Federal de Sergipe, 49100-000, Aracaju — SE, Brazil
[d]Departamento de Fisica, Universidade Federal de Campina Grande, 58429-900, Campina Grande — PB, Brazil
[e]Departamento de Fisica, Universidade Federal do Rio Grande do Norte, 59078-970, Natal — RN, Brazil
E-mail: montirana1992@gmail.com, djain@ddu.du.ac.in, shobhit.mahajan@gmail.com, amimukh@gmail.com, holanda@uepb.edu.br

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Abstract. The construction of the cosmic distance-duality relation (CDDR) has been widely studied. However, its consistency with various new observables remains a topic of interest. We present a new way to constrain the CDDR $\eta(z)$ using different dynamic and geometric properties of strong gravitational lenses (SGL) along with SNe Ia observations. We use a sample of 102 SGL with the measurement of corresponding velocity dispersion σ_0 and Einstein radius θ_E. In addition, we also use a dataset of 12 two image lensing systems containing the measure of time delay Δt between source images. Jointly these two datasets give us the angular diameter distance $D_{A_{ol}}$ of the lens. Further, for luminosity distance, we use the 740 observations from JLA compilation of SNe Ia. To study the combined behavior of these datasets we use a model independent method, Gaussian Process (GP). We also check the efficiency of GP by applying it on simulated datasets, which are generated in a phenomenological way by using realistic cosmological error bars. Finally, we conclude that the combined bounds from the SGL and SNe Ia observation do not favor any deviation of CDDR and are in concordance with the standard value ($\eta = 1$) within 2σ confidence region, which further strengthens the theoretical acceptance of CDDR.

Keywords: gravitational lensing, supernova type Ia - standard candles, dark energy experiments, dark energy theory

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[1]Corresponding author.

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Bounds on graviton mass using weak lensing and SZ effect in galaxy clusters

Akshay Rana [a,*], Deepak Jain [b], Shobhit Mahajan [a], Amitabha Mukherjee [a]

[a] Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India
[b] Deen Dayal Upadhyaya College, University of Delhi, Sector-3, Dwarka, New Delhi 110078, India

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ABSTRACT

In General Relativity (GR), the graviton is massless. However, a common feature in several theoretical alternatives of GR is a non-zero mass for the graviton. These theories can be described as massive gravity theories. Despite many theoretical complexities in these theories, on phenomenological grounds the implications of massive gravity have been widely used to put bounds on graviton mass. One of the generic implications of giving a mass to the graviton is that the gravitational potential will follow a Yukawa-like fall off. We use this feature of massive gravity theories to probe the mass of graviton by using the largest gravitationally bound objects, namely galaxy clusters. In this work, we use the mass estimates of galaxy clusters measured at various cosmologically defined radial distances measured via weak lensing (WL) and Sunyaev–Zel'dovich (SZ) effect. We also use the model independent values of Hubble parameter $H(z)$ smoothed by a non-parametric method, Gaussian process. Within 1σ confidence region, we obtain the mass of graviton $m_g < 5.9 \times 10^{-30}$ eV with the corresponding Compton length scale $\lambda_g > 6.82$ Mpc from weak lensing and $m_g < 8.31 \times 10^{-30}$ eV with $\lambda_g > 5.012$ Mpc from SZ effect. This analysis improves the upper bound on graviton mass obtained earlier from galaxy clusters.

1. Introduction

General theory of Relativity (GR) is one of the most elegant theories of gravity. It had been introduced only on the basis of theoretical principles before being tested and confirmed by observations [1]. Till date all of its predictions have been tested and verified in different limits [2]. In the weak field approximation, observations like the precise measurement of the perihelion advance of Mercury [3], deflection of light by the Sun [4], gravitational time delay [5], equivalence principle [6], the Nordtvedt effect in lunar motion [7], frame-dragging [8] etc., show an impeccable agreement with the observations at solar system length scales [9]. The recent detection of gravitational waves [10] as well as time lag measurements on binary radio pulsar [11] verified the consistency of GR even in the strong field limit [12]. However, there is still a lack of direct observations at large length scales ($\sim$ Mpc) that can establish the consistency of GR [13]. Further, there is a need to introduce a dark component in the energy budget of the Universe to make it compatible with cosmological observations [14]. This dark sector of the Universe remains unobserved which in turn could be taken as an opportunity to look for alternatives to GR at large (cosmological) length scales. The study of any deviation and modification of GR remains an exciting topic of research and has immense theoretical importance. Many alternative theories like $f(R)$ gravity [15], Chameleon theory [16], Galileon models [17] etc., have been proposed. For a detailed review of alternative theories of gravity, see ref. [18–20].

Massive gravity theories are a class of alternative theories to GR that can explain the cosmic acceleration without invoking a dark component in the Universe [21,22]. In 1939, Fierz and Pauli (F&P) proposed a very elegant theory of massive spin 2 gravitons, in which they added a mass term to the Einstein–Hilbert action in such a way that GR is recovered when the mass term tends to zero [23]. However, this theory of massive gravity failed to reproduce the results of GR at small scales (specially at solar system scales). This incompatibility is known as van Dam, Veltman, and Zakharov (vDVZ) discontinuity (1970) in literature [24]. But Vainshtein (1972) presented a mechanism where he showed that the vDVZ discontinuity can be cured by taking into account non-linearities [25]. Soon thereafter, Boulware and Deser (1972) found that a ghost-like negative kinetic term appears in the non-linear

* Corresponding author.
E-mail address: aksrana92@gmail.com (A. Rana).

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Gender perception in the development of online legal information system for the Indian environment

Raj Kumar Bhardwaj
St Stephen's College, University of Delhi, Delhi, India

Abstract

Purpose – The study aims to identify gender differences and similarities in the awareness of legal information resources and problems faced by legal professionals. Further, the study identifies the differences on the basis of gender, regarding the requirements in developing an online legal information system (OLIS) for the Indian environment.

Design/methodology/approach – The study was carried out in eight law libraries in Delhi using a structured questionnaire. Data were collected through the questionnaire having 27 questions including dichotomous (Yes/No), multiple-choice questions, rating and opinion questions. A need assessment survey was conducted using the structured questionnaire circulated among 750 respondents of eight institutions in Delhi. In total, 397 filled in questionnaires were received back. A total of 246 of the respondents were males and 151 females. The design and development of an OLIS went through five phases, i.e. preliminary preparation, designing and planning phase, development of OLIS covering preparation of software, data structures, metadata, search form, testing and implementation phase and maintenance.

Findings – The study found that 100 per cent of the female respondents were aware of online legal information resources. Maximum 28.4 per cent female respondents rated legal e-resources "very good", whereas only 19.9 per cent male ranked them "very good". Female respondents were found less aware about open access resources. In addition, of 246 male respondents, 213 (86.6 per cent) responded "Yes" about awareness of open access resources and 33 (13.4 per cent) marked "No". In comparison, 116 (76.8 per cent) female respondents revealed they are aware of open access resources; 35 (23.2 per cent) were not aware of open access resources. Fifty-eight (23.6 per cent) male respondents were very dissatisfied, and 60 (24.4 per cent) completely dissatisfied. However, in contrast, 29 (19.2 per cent) female respondents were very dissatisfied and 24 (15.9 per cent) completely dissatisfied in using open access resources.

Research limitations/implications – The study covers only eight institutions in Delhi, India. High courts and law universities in other parts of the country are not covered. In addition, OLIS contains a sample collection.

Practical implications – The study explores the inhibitions faced by female and male legal professionals. A suitable legal information system is developed to match the requirements of female legal professionals, research scholars and faculty members. The study is expected to address problems faced by female legal professionals in accessing the desired judicial and legislative information.

Originality/value – OLIS (www.olisindia.in) has been developed on the basis of a need assessment survey conducted on male and female legal professionals in India. No study has been conducted so far to compare the viewpoints of male and female legal professionals in India for developing an OLIS.

Keywords Information system, Judicial information, Law libraries, Legal information, Open access resources, Women lawyers

Paper type Research paper

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Mapping of global research literature in the field of cloud computing

Raj Kumar Bhardwaj

Cloud computing services mark a new paradigm shift in attracting business models for high level customer satisfaction. It empowers users to virtually use the computing servers anytime, irrespective of location. The present study analyzed the dataset obtained from Scopus (http://www.scopus.com) on various aspects of cloud computing to map progress in the field. The study found that 4108 papers have been published on cloud computing till December 31, 2013. These papers have been cited 38339 times till December 31, 2014. The average number of publications per year has been ~684.7. Maximum literature has been published in English, 3598 (87.6 percent) and Chinese, 416 (10.1 percent). Literature on the subject was published in 157 journals around the world. Overall, 95 countries contributed to producing the literature on cloud computing. China is the leading country in publishing cloud computing research with 1208 papers (29.4 percent). Using the Salton's index the collaboration was found strong between Spain and United Kingdom (~0.1139), United Kingdom and Germany (~0.0957). 21 highly cited papers accounted for total 9595 (25.0 percent) citations. It is noted that 1422 (34.6 percent) papers have not been cited by any author. The study revealed that 160 institutes around the globe contributed on the subject. Beijing University of Posts and Telecommunications is the leading institutes with 80 (1.9 percent) papers. Buyya, R. from University of Melbourne is the leading author in the subject with 27 (0.7 percent) papers and his papers received the highest citations 2734 (3.4 percent). The journal entitled 'Future Generation Computer Systems' published the highest number of papers, 75 (1.8 percent) and received the highest citations, 2961 (7.7 percent).

Keywords: *Cloud Computing, Virtual Computing, Bibliometric Study, Contents Analysis, Journal Citations Report (JCR), SCImago Journal Rank (SJR), Source Normalized Impact per Paper (SNIP), Salton's Index, Salton's cosine, Salton's Measure*

Raj Kumar Bhardwaj
Library
St. Stephen's College
Delhi-110007
India

raajchd@gmail.com

A comprehensive digital environment for visually impaired students: user's perspectives

Raj Kumar Bhardwaj
Department of Library, St Stephen's College, University of Delhi, Delhi, India, and
Sanjay Kumar
Department of Physics, St Stephen's College, University of Delhi, Delhi, India

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Abstract

Purpose – The purpose of this paper is to understand the perception of visually impaired undergraduate students about the digital environment in their institutions and develop an online information system suiting their requirements.

Design/methodology/approach – A survey was conducted on undergraduate students enrolled in ten colleges of the University of Delhi. A total of 95 visually impaired students were interviewed individually. Data collected from the respondents were analyzed and interpreted using simple percentage method and is presented in the form of figures.

Findings – The study found that maximum (35.8 percent) respondents access online electronic resources daily. Major constraints faced by them are as follows: inaccessibility of the college notice board, lack of accessibility to existing facilities and resources, lack of assistive technology facilities and unavailability of readers and writers. In total, 51.6 percent respondents indicated that it is cumbersome to access the college website because they are not designed according to the accessibility standards developed for visually impaired students. The respondents also revealed that they are not very familiar with useful devices like Vachak (Hindi Reading Device), SARA CE, Lex (Scanner for Hindi Script). The major reason cited by them is the lack of training and non-availability of trained staff.

Research limitations/implications – DigitVaran contains course contents of the University of Delhi. Course contents of other Universities are not included. However, it is expected that contents related to the syllabi of other universities would be added in future.

Practical implications – The study will help visually impaired students to get the desired course contents conveniently. In addition, librarians of other universities can utilize the findings of the study to develop a comprehensive digital environment for visually impaired students. The study can be helpful in the assessment of digital infrastructure and services to visually impaired students by National Assessment and Accreditation Council and other funding agencies.

Originality/value – The study developed an information system DigitVaran to assist visually impaired undergraduate students in India. The system will help them to access the study materials and make aware of various extracurricular activities of the institutions.

Keywords Blind, E-resources, Web accessibility, Visually impaired, Digital infrastructure, DigitVaran

Paper type Research paper

1. Introduction

Visually impaired students encounter several barriers in daily life and frequently require the use of assistive tools and technologies in their studies (Creed, 2016). These students do not have the same opportunities compared to normal students. An estimated 37 million people in the world are blind, of whom over 15 million are from India (*Times of India*, 2007). It is reported that at least 5 percent, and possibly up to 10 percent, of all Americans have some type of print disability (Petri, 2012). Normal students access several social networking sites to get the desired information, while visually impaired students in developing and under

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Research Activities of Library and Information Science Professionals in Indian Higher Educational Institutions: Competencies, Support and Engagements

Raj Kumar Bhardwaj

St Stephen's College, University of Delhi, Delhi-110 007
E-mail: raajchd@gmail.com

ABSTRACT

The present study is an attempt to understand the research attitude, engagement and competencies of LIS professionals in higher educational institutions in India. It was found that out of 170 respondents, 145 (85.3%) respondents read research literature regularly and 75 (44.1) expressed that reading research based articles is their regular activity. But 95 (55.9) do not read journal articles. 155 (91.2) respondents revealed that they have conducted research after obtaining the formal degree. Majority of respondents 47 (27.6) revealed that their preferred mode of dissemination of research has been publishing paper in conference proceedings, followed by publishing a paper in refereed journals 35 (20.6). Maximum respondents 72 (40.0) followed a theoretical approach in conducting research, followed by survey method 55 (30.6). 'E-resources' (160) and 'Bibliometric Study' (120) has been the most preferred areas of research publishing. 'Lack of funding support' (160), 'time constraints' (155) and 'Problems in data collection' (150), have been identified as major constraints in carrying out research. The main purpose for conducting research is to find the academic performance indicators (APIs) 150, followed by personal growth (102). The study suggests that funding agencies and universities need to come forward to encourage LIS professionals to pursue research and publishing. This will add value in delivering the best library services to academic community and also improve research activities in academic institutions.

Keywords: Research competencies, research involvements, librarians, research activities, universities, India

1. INTRODUCTION

Professionals have been arguing for long whether library professionals should pursue publication despite heavy professional and administrative responsibilities. Some people believe that librarians are ill-prepared for conducting research and enormous work pressure does not allow them to conduct research. Undoubtedly, conducting research by library professionals is crucial and utmost needed to enhance day to day problem solving and better decision making in libraries. In addition, it makes librarians critical consumers of research publications and equips them to provide efficient information services to research scholars and faculty members. Therefore, hindrances faced by academic librarians need to be identified to overcome their problems. It is essential for academic librarians to read and apply the findings of the study in daily library operations. It is also imperative to know whether exiting research literature impacts their own area of study. Academic librarians consider and ponder upon their own work and the research questions that arise. Librarians must strive to bridge the gap between research and practice so that library resources can be utilised optimally and users can get the best services. Library and information science research is equally important for the education system and the growth of LIS research. Majority of research conducted in the field are published in National journals. For global visibility, research in the subject should be published in International journals as well[4]. We need to enhance the engagement of practioner librarians in contributing to research publication. It will help us minimise the gap between research and practice. Supporting the research of academic librarians is important and strongly recommended by professionals. Studies reveal that research helps librarians in career development. The present study is an attempt to understand the attitude and engagement towards research among library professionals in academic libraries in India.

2. LITERATURE REVIEW

Several studies related to library and information science research, research skills and attitude of librarians were reviewed. Berg, Jacobs Cornwall[1] discussed about viewpoint of library administrators in Canadian Association of Research Libraries (CARL) regarding research in library functioning particularly in academic librarianship. The study found that university librarians' expectations from research are inconsistent and only a few institutions provide documentation outline in a formal way. Furthermore, the study found lack of understanding among library professional about the recent research practices occurring across Canadian academic libraries. Bolin[2] found in her study that some librarians consider demands of research writing irrational and tedious. Furthermore, it states, 'a contingent of authors and librarians feel librarians are ill-prepared to take on research due to lack of education in research skills'. The major reason of lack of research

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Enzymatic separation of epimeric 4-*C*-hydroxymethylated furanosugars: Synthesis of bicyclic nucleosides

Neha Rana, Manish Kumar, Vinod Khatri, Jyotirmoy Maity and Ashok K. Prasad*

Full Research Paper

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Address:
Bioorganic Laboratory, Department of Chemistry, University of Delhi, Delhi-110 007, India; Phone: 00-91-11-27662486

Email:
Ashok K. Prasad* - ashokenzyme@gmail.com

* Corresponding author

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Abstract

Conversion of D-glucose to 4-*C*-hydroxymethyl-1,2-*O*-isopropylidene-α-D-ribofuranose, which is a key precursor for the synthesis of different types of bicyclic/spiro nucleosides, led to the formation of an inseparable 1:1 mixture of the desired product and 4-*C*-hydroxymethyl-1,2-*O*-isopropylidene-α-D-xylofuranose. A convenient environment friendly Novozyme®-435 catalyzed selective acetylation methodology has been developed for the separation of an epimeric mixture of ribo- and xylotrihydroxyfuranosides in quantitative yields. The structure of both the monoacetylated epimers, i.e., 5-*O*-acetyl-4-*C*-hydroxymethyl-1,2-*O*-isopropylidene-α-D-ribo- and xylofuranose obtained by enzymatic acetylation, has been confirmed by an X-ray study on their corresponding 4-*C*-*p*-toluenesulfonyloxymethyl derivatives. Furthermore, the two separated epimers were used for the convergent synthesis of two different types of bicyclic nucleosides, which confirms their synthetic utility.

Introduction

Sugar-modified bicyclic nucleosides have drawn the attention of synthetic chemists because of their effect on the conformational restriction of the furanose moiety of the nucleoside [1-9]. The conformational restriction has led to the enhancement in target selectivity and in vivo stability of the nucleoside-based drug candidates. One of the important precursors for the synthesis of different types of bicyclonucleosides is 4-*C*-hydroxymethyl-1,2-*O*-isopropylidene-α-D-ribofuranose. The synthesis of the ribo-trihydroxy sugar derivative starting from diacetone-D-glucose led to the formation of an inseparable 1:1 mixture of the required compound and its C-3 epimer, i.e., 4-*C*-hydroxymethyl-1,2-*O*-isopropylidene-α-D-xylofuranose [10].

Lipases have been used extensively for the selective manipulation of hydroxy groups present in different sugars and sugar moieties of synthetic or naturally occurring glycosides, nucleosides, etc. Gotor et al. [11] have reported a lipase-mediated

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RESEARCH ARTICLE

Biocatalytic route to *C*-4′-spiro-oxetano-xylofuranosyl pyrimidine nucleosides

Pallavi Rungta, Priyanka Mangla, Vinod Khatri, Jyotirmoy Maity and Ashok K. Prasad

Department of Chemistry, Bioorganic Laboratory, University of Delhi, Delhi, India

ABSTRACT

A facile access to *C*-4′-spiro-oxetano-xylofuranosyl nucleosides has been demonstrated for the first time through Lipozyme® TL IM-mediated regioselective acetylation of one of the primary hydroxyl group over the other primary and secondary hydroxyl groups in 3′-*O*-benzyl-4′-*C*-hydroxymethyl-β-D-xylofuranosyl nucleosides. Attempts to optimize a convergent route for these spironucleosides via selective manipulation of hydroxyl groups in 3-*O*-benzyl-4-*C*-hydroxymethyl-1,2-*O*-isopropylidene-α-D-xylofuranose were unsuccessful. Nevertheless; the present linear biocatalytic route efficiently afforded the *C*-4′-spiro-oxetanoxylofuranosyl nucleosides T and U in 47 and 38% overall yields, respectively, starting from corresponding furanose diol.

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Biocatalysis; regioselective acetylation; spiro-nucleosides

1. Introduction

Chemical modifications of the sugar functionality in nucleosides have continuously reflected its supremacy for the treatment of cancer and viral infections over the past 50 years (De Clercq 2011; Prakash 2011; Sofia et al. 2012; Jordheim et al. 2013; Sharma et al. 2014a, 2014b). Among the studied sugar-modified nucleosides, spironucleosides had only little impact and progress until the recent finding that these are selective and potent inhibitors of Hepatitis C Virus (HCV) (Dang et al. 2014a, 2014b; Du et al. 2014; Jonckers et al. 2010, 2014). The presence of spiro-carbon in nucleosides imparts restriction to the conformational flipping of furanose ring and thus can modulate or enhance their selectivity and biological activity. This has prompted the synthesis of all possible classes of spironucleosides, e.g. *C*-1′-spiro-(Maza et al. 2009; Pal and Yashwant 2010), *C*-2′-spiro-(Du et al. 2014; Dang et al. 2014b; Jonckers et al. 2010, 2014), *C*-3′-spiro-(Camarasa et al. 1992; De Castro et al. 2007; Das et al. 2011) and *C*-4′-spironucleosides (Paquette et al. 2003; Paquette 2004; Paquette et al. 2004; Dong and Paquette 2005; Dong and Paquette 2006; Roy et al. 2006; Dang et al. 2014a; Sharma et al. 2014c; Kumar et al. 2015; Kumar et al. 2017); and many of them have shown excellent antiviral activity (Figure 1). Prominent among them are the *C*-4′-spironucleosides which display distinct sugar conformation (Paquette 2004). In order to scrutinize the presence of the spiro- and the oxetano-systems in a nucleoside, attempts have been made to install oxetano-spiro cyclization at *C*-4′-position in xylofuranosyl nucleosides ((Sharma et al. 2014a), Figure 1) that have earlier turned out to be futile (Roy et al. 2006). Our group has earlier demonstrated the synthesis of various *C*-4′-spiro-oxetano-ribonucleosides (Sharma et al. 2014c; Kumar et al. 2015, 2017). Kumar et al. optimized Novozyme®-435 mediated regio-selective deacetylation of *C*-5 acetoxy group in 5-*O*-acetyl-4-*C*-acetyloxymethyl-3-azido-1,2-*O*-isopropylidine-α-D-ribofuranose to establish a methodology for successful synthesis of *C*-4′-spiro-oxetano-β-D-ribonucleosides (Kumar et al. 2015). In another venture, Kumar et al. successfully used Lipozyme® TL IM-catalyzed acylation on *C*-4′-hydroxymethyl-β-D-xylofuranosyl nucleosides and synthesized structurally novel *C*-4′-spiro-oxetano-α-L-ribonucleosides (Kumar et al. 2017). In the present communication, we have reported the first synthesis of *C*-4′-spiro-oxetano-xylofuranosyl nucleosides that is devised by the mediation of Lipozyme® TL IM, an immobilised *Thermomyces lanuginosa* lipase.

2. Experimental section

Materials. Analytical TLCs were performed on precoated Merck silica gel $60F_{254}$ plates; the spots were detected either using UV light or by charring with 4% alcoholic sulphuric acid. The optical rotations were measured on Rudolph autopol II automatic polarimeter using light of 546 nm wavelegth. The melting points

CONTACT Ashok K. Prasad ashokenzyme@gmail.com Bioorganic Laboratory, Department of Chemistry, University of Delhi, Delhi, India
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Research paper

Synthesis and antimycobacterial activity of 1-(β-D-Ribofuranosyl)-4-coumarinyloxymethyl- / -coumarinyl-1,2,3-triazole

Smriti Srivastava [a, 1], Devla Bimal [a, 1], Kapil Bohra [a, b], Balram Singh [a], Prija Ponnan [a], Ruchi Jain [a], Mandira Varma-Basil [c], Jyotirmoy Maity [a], M. Thirumal [a], Ashok K. Prasad [a, *]

[a] Department of Chemistry, University of Delhi, Delhi-110007, India
[b] Department of Chemistry, Deen Dayal Upadhyaya College, University of Delhi, Delhi-110078, India
[c] Department of Microbiology, VP Chest Institute, University of Delhi, Delhi-110007, India

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ABSTRACT

A series of β-D-ribofuranosyl coumarinyl-1,2,3-triazoles have been synthesized by Cu-catalyzed cycloaddition reaction between azidosugar and 7-*O*-/7-alkynylated coumarins in 62–70% overall yields. The *in vitro* antimycobacterial activity evaluation of the synthesized triazolo-conjugates against *Mycobacterium tuberculosis* revealed that compounds were bactericidal in nature and some of them were found to be more active than one of the first line antimycobacterial drug ethambutol against sensitive reference strain H37Rv, and 7 to 420 times more active than all four first line antimycobacterial drugs (isoniazid, rifampicin, ethambutol and streptomycin) against multidrug resistant clinical isolate 591. Study of *in silico* pharmacokinetic profile indicated the drug like characters for the test molecules. Further, transmission electron microscopic experiments revealed that these compounds interfere with the constitution of bacterial cell wall possibly by targeting mycobacterial InhA and DNA gyrase enzymes. Study conducted on the activities of the test compounds on bacterial InhA and DNA gyrase revealed that the most bactericidal test compound, N^1-(β-D-ribofuranosyl)-C^4-(4-methylcoumarin-7-oxymethyl)-1,2,3-triazole (**6b**) and its corresponding directly linked conjugate N^1-(β-D-ribofuranosyl)-C^4-(4-methylcoumarin-7-yl)-1,2,3-triazole (**11b**) significantly inhibited the activity of both the enzymes. The results were further supported by molecular docking studies of the compound **6b** and **11b** with bacterial InhA and DNA gyrase B enzymes. Further, the cytotoxicity study of some of the better active compounds on THP-1 macrophage cell line using MTT assay showed that the synthesized compounds were non-cytotoxic.

1. Introduction

There is a great need for the development of newer molecular entities to act as antimycobacterial agents due to the limitations of the existing drugs as well as the increasing resistance against causative bacteria, *Mycobacterium tuberculosis* (*M. tuberculosis*) [1–4]. In HIV-prevalent regions, infection by drug-resistant tuberculosis (TB) almost always has fatal consequences [5,6]. Drugs that are effective in reducing the length of treatments providing effective cure against multi-drug resistant TB (MDR), extremely drug resistant TB (XDR) and latent TB is the requirement of the time [2,3].

Carbohydrates are among the most ample raw materials provided by nature, which play a significant role at the interface of chemistry and biology [7,8]. On the other hand coumarins and their derivatives have shown their potential as antitubercular [1], anticancer [9–12], anti-HIV [13], anti-inflammatory [14,15], antifungal [16], anti-oxidant [14,15], and anti-bacterial agents [17a]. Several coumarin derivatives, such as warfarin, carbochromen and acenocoumarol have been approved by FDA for their clinical therapeutic uses [17a-c]. Both, the sugar and the coumarin moieties are excellent biomolecules and have wide variety of applications as well as good biocompatibility [18,19]. There are few reports of synthesis of conjugates of sugar-coumarin or sugar-quinoline linked through a triazole ring that have shown interesting biological activities (Fig. 1) [17d, 17e, 20–25]. We report herein the

* Corresponding author. Bioorganic Laboratory, Department of Chemistry, University of Delhi, Delhi-110 007, India.
E-mail address: ashokenzyme@gmail.com (A.K. Prasad).
[1] First and second author contributed equally to this work and should be regarded as joint First authors.

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Synthesis of novel 3′-azido-3′-deoxy-α-L-*ribo* configured nucleosides: A comparative study between chemical and chemo-enzymatic methodologies

Neha Rana, Manish Kumar, Ankita Singh, Jyotirmoy Maity, Poonam Shukla, and Ashok K. Prasad

Bioorganic Laboratory, Department of Chemistry, University of Delhi, Delhi, India

ABSTRACT

Syntheses of novel 3′-azido-3′-deoxy-2′-*O*,4′-*C*-methylene-α-L-*ribo*furanosyl nucleosides have been carried out from 3′-azido-3′-deoxy-4′-C-hydroxymethyl-β-D-*xylo*furanosyl nucleosides following both chemical and chemo-enzymatic methodologies. The precursor nucleoside in turn was synthesized from a common glycosyl donor 4-*C*-acetoxymethyl-1,2,5-tri-*O*-acetyl-3-azido-3-deoxy-α,β-D-*xylo*furanose, which was obtained by the acetolysis of 4-*C*-acetoxymethyl-5-*O*-acetyl-3-azido-3-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*furanose in 96% yield. It has been observed that a chemo-enzymatic pathway for the synthesis of targeted nucleosides is much more efficient than a chemical pathway, leading to the improvement in yield for the synthesis of 3′-azido-3′-deoxy-α-L-*ribo*furanosyl thymine and uracil from 49 to 89% and 55 to 93%, respectively.

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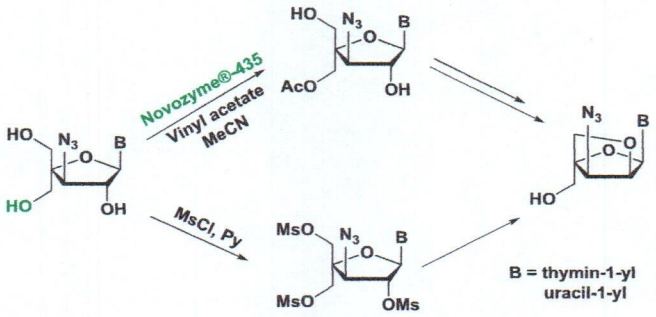
diastereoselective; biocatalysis; novozyme®-435; 3′-azido-3′-deoxy-α-L-*ribo*furanosyl nucleosides

GRAPHICAL ABSTRACT



Introduction

There has been a surge in the synthesis of conformationally constrained sugar modified nucleosides and nucleotides for the development of target specific gene

CONTACT Ashok K. Prasad ashokenzyme@gmail.com Bioorganic Laboratory, Department of Chemistry, University of Delhi, Delhi-110 007, India.
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lncn.

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Synthesis of novel 3-[(1-glycosyl-1*H*-1,2,3-triazol-4-yl)-methylamino]ket-2-en-1-ones

Banty Kumar[1,2], Jyotirmoy Maity[1], Amit Kumar[1], Vinod Khatri[1], Bhawani Shankar[1], Ashok K. Prasad[1]*

[1] *Bioorganic Laboratory, Department of Chemistry, University of Delhi, Delhi 110 007, India; e-mail: ashokenzyme@gmail.com*

[2] *Rajdhani College, Department of Chemistry, University of Delhi, Delhi 110 007, India; e-mail: bantykumar881@gmail.com*

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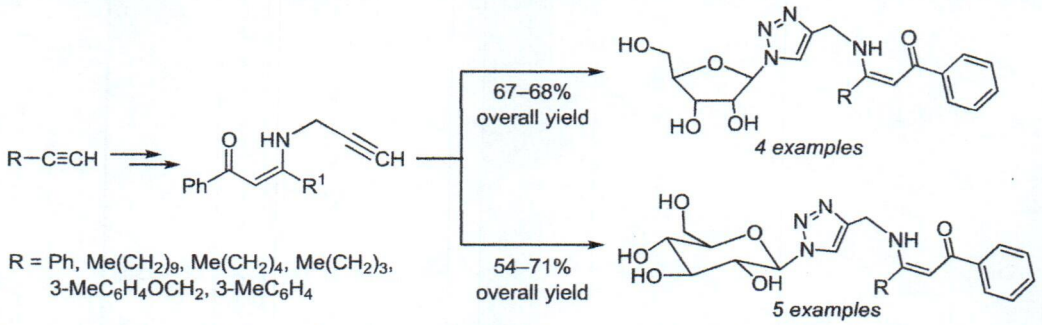

Nine 3-[(1-β-D-ribofuranosyl- and 3-[(1-β-D-glucopyranosyl-1*H*-1,2,3-triazol-4-yl)methylamino]ket-2-en-1-ones have been synthesized by copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction between propargylamine derivatives and 1-azido-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose or 2,3,4,6-tetra-*O*-acetyl-1-azido-β-D-glucopyranose, followed by deprotection of the resulting tri-*O*-benzoyl- or tetra-*O*-acetyl-1-β-D-glycosyltriazoles in good yields. The precursor propargylamine derivatives were synthesized by Sonogashira reaction of substituted acetylenes and benzoyl chloride followed by Michael-type addition of propargylamine to the resulting substituted alkynes in good yields. The precursor azido sugars, 1-azido-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose and 2,3,4,6-tetra-*O*-acetyl-1-azido-β-D-glucopyranose, were synthesized by azidation of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose and β-D-glucopyranose pentacetate, respectively, with azidotrimethylsilane in the presence of tin(IV) chloride. All products were unambiguously characterized on the basis of the spectral data analysis.

Keywords: *N*-glycoconjugates, CuAAC reaction, Sonogashira reaction.

Carbohydrates and glycoconjugates are involved in numerous biologically and pathologically significant regulatory processes,[1] such as immune response, cell-cell recognition, interaction of pathogen and host, cell adhesion,[2] cancer and metastasis,[3] inflammation,[4] etc. Due to their prominent role in biology and medicine, efforts are being directed toward the development of novel carbohydrate-based scaffolds with desirable properties. Further, due to the relevance of the click chemistry in the recent past, 1,2,3-triazole cycle has emerged as a promising heterocyclic aglycon moiety. There are ample examples in the literature on glycosyl triazoles and broad spectrum of their chemical and biological significance.[5,6] They are reported as inhibitors of galectin proteins,[7] glycogen phosphorylase,[8] carbonic anhydrase,[9] sweet almond β-glucosidase[10] and as anticancer agents.[11] Herein, we report the synthesis of novel 3-[(1-glycosyl-1*H*-1,2,3-triazol-4-yl)methylamino]ket-2-en-1-ones *via* copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction of 1-azido-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose or 1-azido-2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose to 1-phenyl-3-propargylaminoprop-2-en-1-ones in good to excellent yield.

The precursors for the synthesis of the targeted 3-[(1-glycosyl-1*H*-1,2,3-triazol-4-yl)methylamino]ket-2-en-1-ones are 1-phenyl-3-propargylaminopropenones **4a–f**, 1-azido-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (**5**) and 2,3,4,6-tetra-*O*-acetyl-1-azido-β-D-glucopyranose (**6**). The alkyne precursors, i.e., 1,3-diphenyl-3-(prop-2-yn-1-ylamino)-prop-2-en-1-one (**4a**), 1-phenyl-3-(prop-2-yn-1-ylamino)-tridec-2-en-1-one (**4b**), 1-phenyl-3-(prop-2-yn-1-ylamino)-oct-2-en-1-one (**4c**), 1-phenyl-3-(prop-2-yn-1-ylamino)hept-

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Microwave dielectrics: solid solution, ordering and microwave dielectric properties of $(1-x)Ba(Mg_{1/3}Nb_{2/3})O_3-xBa(Mg_{1/8}Nb_{3/4})O_3$ ceramics

YOGITA BISHT[1], RICHA TOMAR[1], PULLANCHIYODAN ABHILASH[2], DEEPA RAJENDRAN LEKSHMI[2] and M THIRUMAL[1,*]

[1]Department of Chemistry, University of Delhi, Delhi 110007, India

[2]Materials Science and Technology Division, National Institute for Interdisciplinary Science and Technology (NIIST-CSIR), Industrial Estate, Trivandrum 695019, India

*Author for correspondence (thirumalm@hotmail.com)

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Abstract. The effect of $Ba(Mg_{1/8}Nb_{3/4})O_3$ phase on structure and dielectric properties of $Ba(Mg_{1/3}Nb_{2/3})O_3$ was studied by synthesizing $(1-x)Ba(Mg_{1/3}Nb_{2/3})O_3-xBa(Mg_{1/8}Nb_{3/4})O_3$ (x = 0, 0.005, 0.01 and 0.02) ceramics. Superlattice reflections due to 1:2 ordering appear as low as 1000°C. $Ba(Mg_{1/3}Nb_{2/3})O_3$ forms solid solution with $Ba(Mg_{1/8}Nb_{3/4})O_3$ for all 'x' values studied until 1350°C. Ordering was confirmed by powder X-ray diffraction pattern, Raman study and HRTEM. Ceramic pucks can be sintered to density >92% of theoretical density. Temperature and frequency-stable dielectric constant and nearly zero dielectric loss (tan δ) were observed at low frequencies (20 MHz). The sintered samples exhibit dielectric constant (ε_r) between 30 and 32, high quality factor between 37000 and 74000 GHz and temperature coefficient of resonant frequency (τ_f) between 21 and 24 ppm $°C^{-1}$.

Keywords. Resonators; complex perovskites; X-ray diffraction; dielectric properties; high Q.

1. Introduction

$Ba(B'_{1/3}B''_{2/3})O_3$ (B′ = Zn, Mg, Ni, Co and B″ = Ta, Nb)-based perovskite oxides are used in microwave dielectrics, which have application in wireless communications. Their high permittivity (ε_r), high quality factor (Q.f.) and near-zero temperature coefficient of resonant frequency (τ_f) make them excellent candidates for filters and resonators at base station. Here, Ta^{5+} and Nb^{5+} are used as transition metal ions with low-lying d^0 orbital mix with the orbital of ligands and create multiple coordination with oxygen [1]. This improves polarizability of these elements and they also provide opportunities of compositional tuning by the substitutional flexibility of B-site cations. Normally, among all the known $Ba(B'_{1/3}B''_{2/3})O_3$ (B′ = Zn, Mg, Ni, Co and B″ = Ta, Nb) perovskites, tantalates show much better Q.f. as compared with niobates. However, Ta^{5+} is comparatively expensive; hence, to reduce the cost of dielectric resonators and to understand the chemistry, niobates are explored as the logical substitute for tantalates. $Ba(Mg_{1/3}Nb_{2/3})O_3$ (BMN) is one such ceramic that draws attention due to its good dielectric properties ε_r = 32, Q = 5600 (10.5 GHz) and τ_f = 33 ppm $°C^{-1}$ [2]. The $A(B_{1/3}B'_{2/3})O_3$-type ceramics have been reported to have three kinds of ordered structures depending upon the arrangement of B-site cations:

(i) disordered cubic structure with space group Pm3m (O^1_h), lattice parameter $a \sim 4$ Å;
(ii) 1:1 ordered cubic structure with space group Fm3m (O^5_h); here, the unit cell lattice parameter is twice that of the disordered cubic structure, i.e., $a \sim 8$ Å;
(iii) 1:2 ordered hexagonal structure with space group P-3m1 (D^3_3d), lattice parameters $a \sim 5.7$ Å and $c \sim 7$ Å.

Among these, 1:2 ordered hexagonal structure is desirable as it is reported to have better Q.f. as compared with others. This kind of 1:2 ordering was first reported by Galasso and Pyle [3] in $Ba(Sr_{1/3}Ta_{2/3})O_3$. They described its structure as a repetition of three close-packed BaO_3 layers with Sr^{2+} and Ta^{5+} in an ordered arrangement with a $\{Sr^{2+}..Ta^{5+}..Ta^{5+}\}$ repeated sequence in octahedral hole. This kind of 1:2 ordering of B-site cations expands the original perovskite unit cell along ⟨111⟩ direction and contracts it along the direction normal to ⟨111⟩, which produces superstructure reflections and deviation of c/a ratio from $\sqrt{3}/2$ (1.2247), the ideal value for hexagonal structure.

It is not easy to observe superlattice reflections related to 1:2 ordering in Nb system as the scattering power of Nb is lower than that of Ta due to lower atomic number of Nb^{5+} than that of Ta^{5+} [4,5]. Galasso and Pyle [6]

نظم 'شکوہ' کا تجزیاتی و موضوعاتی مطالعہ

ڈاکٹر شمیم احمد

سینٹ اسٹیفنز کالج، دہلی یونیورسٹی، دہلی

اقبال روایت شناس شاعر تھے اور روایت شکن بھی۔ روایتیں جب قلب و نظر کا حصہ بن جاتی ہیں تو انسانی بصیرت انھیں آگے بڑھاتی ہے، انھیں ترقی اور بلندی عطا کرتی ہے۔ بلندی کے اس سفر سے پرانی روایتیں ترک ہوتی ہیں اور نئی روایتیں وجود میں آتی ہیں، لیکن یہ نئی روایتیں بالکل نئی نہیں ہوتیں بلکہ ان کی جڑیں پرانی روایتوں میں پیوست ہوتی ہیں۔ اقبال کا تمام کلام انہی نئی اور پرانی روایتوں کے بیچ بین سفر کرتا ہے اور اپنی تاثیر میں اضافہ کرتا ہے۔ وہ غالب کے الفاظ میں ایسے موحد ہیں جن کا کیش ترک رسوم ہے۔ وہ جانتے ہیں کہ ملتیں جب اپنی انا کی تسخیر کے عمل سے گزرتی ہیں تو جزو ایماں بن جاتی ہیں۔ اسلام محض جدی اور روحانی عبادات کا نام نہیں، یہ محض اپنی انفرادی زندگی کو جلا بخشنے کی غرض سے ذکر الٰہی میں مشغول ہونے کا نام نہیں، اسلام اجتماعی زندگی میں شریک ہونے اور تمام انسانوں کی زندگی کو منور کرنے کی کوشش کا نام ہے۔ اقبال کو احساس ہے کہ روح جلال گر نہ ہو تو اذان محض ایک رسم ہے اور اسلام یہ مطالبہ کرتا ہے کہ اس کی طے کردہ عبادات کو رسم سمجھ کر ادا نہ کیا جائے بلکہ انھیں تطہیر قلب کا ذریعہ بنایا جائے۔

شعبہ خاطر پریشانی میں جبکہ اقبال خود کو ایک ایسا بلبل سمجھتے ہوئے جو اب تک خوش نغمہ ہے اور جس کے سینے میں اب تک نغموں کا تلاطم ہے روایت شکنی کا ایسا حوصلہ مجتمع کرنے میں کامیاب ہوتے ہیں کہ خدا سے شکوہ کر سکیں۔ اس شکوے کا اظہار ایک نظم کی صورت میں ہوا اور اپریل 1911ء میں انجمن حمایت اسلام لاہور کے جلسے میں یہ نظم پڑھ کر سنائی گئی۔ یہ جلسہ ہوا ہو شمل اسلامیہ کالج کے احاطے میں منعقد ہوا تھا۔ نظم خلاف معمول پہلے سے چھپی ہوئی نہیں تھی۔ اس کے بعد نظم کا مسودہ فروخت کے لیے لوگوں نے خوب بڑھ چڑھ کر بولیاں لگائی تھیں۔ بعد میں یہ نظم پنجاب ریویو، ماہنامہ مخزن اور دوسرے جرائد میں شائع ہوئی۔

نظم مسدس کی ہیئت میں ہے۔ چھ چھ مصرعوں پر مشتمل بند میں ابتدائی چار مصرعے ایک قافیہ اور ردیف میں ہیں اور آخری دو مصرعے نئے قافیے اور ردیف کے ساتھ نمودار ہوتے ہیں۔ اس سے نظم کے آہنگ اور ترنم میں اضافہ ہوتا ہے۔ نظم میں کل اکتیس بند ہیں۔

نظم کی ابتدا میں اقبال کا مزاج اور آہنگ مرثیہ نگاری اور سراپا نگاری کی جانب آمادہ ہے۔ وہ انتہائی پر اعتماد لہجے میں کسی روٹھے ہوئے نوجوان کی طرح سوال کرتے ہیں کہ دوسری قوموں کے لوگ اپنی اصل رقم پر خوب سود کھاتے ہیں اور زیادہ سے زیادہ دولت مند ہوتے چلے جاتے ہیں جبکہ مسلمان قوم کو اس کی اجازت نہیں۔ اس لیے مسلمان اپنی اصل رقم پر سود نہیں لیتے اور نقصان سہہ جاتے ہیں۔ انھیں یہ تلقین کی گئی ہے کہ مستقبل کی تیاری کے بجائے آج کو سنوارنے میں دلچسپی لیں۔ سوال یہ ہے کہ ان حدود کی پابندی صرف مسلمانوں تک کیوں محدود ہے اور یہ سوالات صرف اقبال کے ذہن میں سر نہیں ابھارتے بلکہ قوم کے نوجوانوں کا یہ شکوہ اقبال کے کانوں تک اکثر پہنچتا رہتا ہے۔ اس لیے اقبال قوم کی نمائندگی کرتے ہوئے اپنی جرأت اور حوصلے کو آزماتے ہیں اور اللہ سے شکوہ کرنے کا بڑا کام اپنے ذمہ لیتے ہیں۔ جس کا نتیجہ سوائے خاکم بدہن بھی کچھ نہیں خاک کے اور کچھ نہیں۔ چوں کہ اقبال کو اپنی جرأت آموزی کا اندازہ ہے اس لیے اگلے بند میں ان کا لہجہ چڑچڑے پن کے بجائے مصالحانہ اختیار کرتا ہے۔ وہ خدا تعالیٰ کے سامنے اپنی مجبوری کا حوالہ دے کر درخواست کرتے ہیں کہ خوگر حمد سے تھوڑا سا گلہ بھی سن لے۔

خود خوگر حمد قرار دے کر اقبال نے یہ اعلان کر دیا ہے کہ یہ عقیدے پر قائم ایک مومن کا مالک حقیقی سے شکوہ ہے۔ یہ ایسا شکوہ نہیں ہے جس میں عقیدے و ایمان کو ترک کرنے کا شائبہ بھی ہو۔ وہ تو بس اپنے ذہن میں آنے والے سوالات کے اظہار کے خواہش مند ہیں۔ شاعر کا حساس دل اپنے جذبات و احساسات کو خود تک محدود رکھنے پر قادر نہیں۔ وہ سراپا سوال بن کر اپنے خالق کے آگے دست سوال دراز کرتے ہیں۔ انھیں یقین ہے کہ اظہار سوال سے ان کی بے قراری میں کمی آئے گی۔ بارگاہ ایزدی سے کوئی ایسا اشارہ موصول ہوگا جو راہ نمائی کا سبب بنے گا۔ اکثر دکھ اور تکلیف کا اظہار ان میں کمی کا باعث بنتا ہے ورنہ بالعکس محض انسان کے لیے مزید ہلاکت کا باعث بن جاتی ہے۔ اقبال اس اندرونی بوجھ کے ساتھ آگے نہیں بڑھنا چاہتے۔ ان کی خواہش ہے کہ اس کا مداوا ممکن ہو جائے۔ کہا جاتا ہے کہ اقبال کے کلام کا تجزیاتی مطالعہ ہمیں یہ راہنمائی عطا کرتا ہے کہ اس نظم میں اپنے شکوک و شبہات

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Defect Induced Ferromagnetism in Zn/ZnO Interfaces

*Mansi Dhingra, Rekha Gupta, and S. Annapoorni**

Zn/ZnO interfaces are prepared by thermal evaporation technique. X-ray diffraction (XRD) and photoluminescence (PL) show the coexistence of both the Zn and ZnO phases which on heat treatment get converted to ZnO. Surface morphologies of the samples are studied using scanning electron microscopy (SEM). It clearly shows formation of granular morphology in pristine sample which gets converted to needle like structures on heating at 500 °C. Magnetic measurements largely hints at the presence of excess Zn in Zn/ZnO interfaces resulting in a ferromagnetic behavior which gradually gets converted to a paramagnetic state on annealing revealing a complete transformation to ZnO. Zinc interstitials lying just below the conduction band forms an impurity state indicates a correlation with magnetic behavior.

1. Introduction

Study of room temperature ferromagnetism in ZnO and transition metal doped ZnO has remained a topic of extensive research as its origin is not yet fully deciphered.[1,2] There are several reports in which ZnO is seen to exhibit ferromagnetism at room temperature when doped with Mn, Co, Cu, Er.[3–6] Doping of Mn in ZnO has been particularly explained theoretically by Dietl et al. but nature of the magnetism in such systems is not fully understood yet.[7] Formation of secondary phases leading to magnetic ordering is one of the chief reasons reported. Different models based on exchange interaction have been formulated. Room-temperature ferromagnetism has even been observed in undoped wide bandgap semiconductors or oxides such as HfO_2, TiO_2, In_2O_3, and ZnO in reduced dimensional forms such as nanoparticles, nanowires, and thin films.[8–10] It has also been reported that defect chemistry in such type of systems plays an important role in triggering room temperature ferromagnetism. However, it is important to understand how these defects facilitate magnetic coupling. Particularly in ZnO, defects like oxygen vacancies (V_O), zinc vacancies (V_{Zn}) and zinc interstitials (Zn_i) are responsible for magnetic behaviour. Wang et al shows that the ferromagnetism in undoped ZnO arises due to the Zn vacancies (V_{Zn}) instead of V_O.[11,12]

Moreover, the defect-related ferromagnetic regions were suggested to be in the bulk, at the surface or interface, or within grain boundaries.[13–16]. Origin of ferromagnetism in interfacial structures has also been studied by different research groups.

Such dilute magnetic semiconductor (DMS) has been used for many applications in spintronic based devices and magnetic tunnel junctions.[17] In present study, Zn/ZnO heterostructure is found to show ferromagnetism at room temperature. We employ a novel method for the fabrication of these heterostructures. These structures help us to understand the transport of charges at the interface of Zn and ZnO. The presence of impurity states at the interfacial region brings about the possible magnetisation.

2. Experimental Section

Zn (99.99% pure) obtained from Sigma Aldrich was thermally evaporated using Thermal evaporation unit (Hind Hivac) at a pressure of 0.01 mbar. Silicon substrates oriented along (100) plane of size 1 cm × 1 cm were placed at a distance of 20 cm from the Zn source. A secondary current of 1A was passed through a molybdenum boat to make all the Zn files evaporate. Thickness of film, as measured using Quartz crystal monitor, was found to be approximately ≈1 μm. The as obtained samples were then annealed at different temperatures viz 100, 300, 500 °C. These films were then subjected to structural, optical and magnetic measurements.

The phase identification was performed in X-ray diffraction technique (XRD) (40 V, 100 mA, D8 Discover-Advanced model of Bruker co. Ltd.) using monochromatic CuKα1 line (λ = 1.54056 Å) and was compared with the available JCPDS data files. The SEM images were taken to study the formation of different morphology (shape and size) of the nanocrystalline material by using scanning electron microscope (SEM ZEISS co. Ltd.) at 20 kV. The magnetic measurements were obtained using Vibrating Sample Magnetometer (VSM). The room temperature photoluminescence (PL) spectra of the sample were measured with a spectrofluorometer (Fluorolog Horiba JOBIN YVON) using λ_{ex} = 350 nm to study different kinds of defects in the material.

3. Structural Analysis

3.1. XRD Studies

Structural analysis was done using XRD at glancing angle mode from 30–60°. **Figure 1** shows XRD pattern of Zn/ZnO films at various temperatures. Figure 1a shows dominant peaks corresponding to Zinc metal. It was seen that as the annealing

Dr. M. Dhingra, Dr. R. Gupta, Prof. S. Annapoorni
Department of Physics and Astrophysics
University of Delhi
Delhi 110007
E-mail: annapoornis@yahoo.co.in

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ORIGINAL PAPER

Magnetization Reversal

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Modelling of Pinning-Depinning Reversal Mechanism in Ion-Irradiated Co/Al_2O_3 Thin Films

*Rajan Goyal, Rekha Gupta, Ambika Negi, Kandasami Asokan, Dinakar Kanjilal, Subhalakshmi Lamba, and Subramanian Annapoorni**

Present study reports the pinning–depinning mechanism in Co embedded Al_2O_3 matrix subjected to Ar^+ ion irradiations. Angular variation studies of the scaled coercivity are carried out and a comparison to existing theoretical models indicates that the dominant reversal mechanism is due to pinning. The origin of pinning is attributed to the displacement of Co atoms from their lattice sites, as a result of ion bombardment. The Monte Carlo simulations suggest that the observed magnetic behavior is well explained by pinning induced strain anisotropy in the system.

1. Introduction

The magnetization reversal mechanism plays a crucial rule in the usefulness of the magnetic materials in various technological applications namely memory devices. Out of several mechanism, pinning is seen to be dominant in defect based magnetic materials. Of the several magnetic NPs, hcp-Co has attracted attention due to its large uniaxial anisotropy ($K_u \approx 0.53$ MJ m^{-3}).[1] The surface oxidation of Co NPs acting as a pinning layer and it result in modification of magnetization reversal mechanism. The mechanism, however, tends to vary with the processing conditions viz. thermal annealing, localized heating by radiation, thickness and composition of nanoparticles as well as on the dielectric matrix surrounding the NPs.[2,3] Embedding metal nanoparticles (NPs) in a dielectric matrix such as Al_2O_3, SiO_2, etc. is an effective way to prevent the oxidation.[4–6] Embedded NPs found attractive applications in magnetic memory devices,[7] biomedicine,[8–9] etc. due to their size dependent structural, optical, and magnetic properties as compared to bulk. Wen et al. reported that the Au-core-Co-shell exhibits enhanced coercivity as compare to pure Co sample, which may be due to the pinning effect of cobalt spins at the Au/Co interface.[10] The dispersion of hcp Co NPs in an amorphous polymer matrix leads to lesser pinning sites resulting in a remarkable reduction in coercivity as compared to that of the polycrystalline pure Co films.[11] Similar behavior was also reported in CoPt alloy consisting of disordered A1 and ordered $L1_0$ phases. The enhancement in coercivity with the increase in volume percentage of $L1_0$ phase was attributed to the presence of local defects such as anti-phase and grain boundaries acting as pinning centers.[12] Akdogan et al also showed that the enhanced coercivity in $SmCo_5$ is probably due to domain wall pinning at grain boundaries and stacking fault.[13] Furthermore, the domain wall pinning in ferromagnetic nanowires can be a potential technique for the fabrication of solid state memory devices. Polenciuc et al. have proposed the fabrication of exchange biased crossed ferromagnetic and antiferromagnetic nanowires to achieve the reproducible domain wall pinning of variable strength by changing the diameter of the antiferromagnetic nanowires.[14]

In our earlier work, we have demonstrated the effect of thermal heat treatment on magnetic anisotropy and depinning field of Co NPs embedded in alumina matrix (Al_2O_3).[15] The Monte Carlo simulation of hysteresis curves revealed that the conventional heat treatment results in uniform distribution of defects throughout the sample leading to a constant pinning field. However, no systematic study has been reported yet to analyze the effect of ion implantation/irradiation on magnetization reversal mechanism in Cobalt NPs embedded in the dielectric matrix. In the present communication, the Co NPs embedded in alumina matrix which remains non-reactive at high annealing temperatures are subjected to ion irradiation using 300 keV Ar^+ ion beam. The structural as well as magnetic analysis, supported by theoretical simulations, are carried out to examine the magnetization reversal mechanism in Co/Al_2O_3 thin films when subjected to low energy ion (LEI) irradiation at different fluences.

2. Experimental Section

The films of Co embedded in Al_2O_3 matrix were deposited on Si <111> single crystal substrate by RF magnetron sputtering. Alumina (Al_2O_3) target of 99.9% purity with Co chips pasted on it in a symmetric fashion was used for depositing the films. The

Dr. R. Goyal, Dr. R. Gupta, Dr. A. Negi, Prof. S. Annapoorni
Department of Physics and Astrophysics
University of Delhi
Delhi 110007, India
E-mail: annapoornis@yahoo.co.in

Dr. K. Asokan, Dr. D. Kanjilal
Inter University Accelerator Center
Aruna Asaf Ali Marg, Delhi-110067, India

Dr. S. Lamba
School of Sciences
Indira Gandhi National Open University
New Delhi 110068, India

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शक्ति विमर्शः न्याय तथा परमलघुमञ्जूषा के सन्दर्भ में

अभय सिंह*

न्यायवैशेषिक दर्शन में शब्द को आकाश का गुण माना जाता है। शब्द का ज्ञान केवल श्रोत्रेन्द्रिय से होता है[1]। श्रोत्र इन्द्रिय से हम सब प्रकार के शब्दो को सुनते हैं। किसी भी प्रकार की आवाज 'शब्द' कही जाएगी, चाहे वह दो पदार्थों के टकराने से उत्पन्न हुई हो, चाहे घण्टा बजने पर अनुरणनरूप हो अथवा किसी जीव के मुख से निकली सार्थक अथवा निरर्थक आवाज हो। **शब्द** के दो प्रमुख भेद किये गये हैं- 1. **वर्ण २. ध्वनि।**

कण्ठ, तालु आदि अवयवों से उच्चरित अकार आदि को 'वर्ण' कहा जाता है। अभिप्राय यह है कि भाषागत अकार आदि वर्ण, उन वर्णों के योग से बने हुए पद तथा पदों से निर्मित वाक्य-महावाक्य सभी वर्ण के अन्तर्गत आते हैं। अर्थात् भाषारूप शब्द को 'वर्ण' कहा जाता है। भाषारूप शब्द को सुनकर हमें अर्थ का ज्ञान होता है। वर्णभिन्न अर्थात् भाषा से भिन्न जो भी शब्द होते हैं वे 'ध्वनि' के अन्तर्गत आते हैं क्योंकि एतादृश ध्वनि अथवा ध्वनिसमूह से हमें अर्थबोध नहीं होता। वैसा अर्थबोध नहीं होता जैसा अर्थबोध भाषागत शब्द (वाक्य) को सुनकर होता है। वर्णरूप शब्द को यदि वह आप्तोक्त है- प्रमाण माना जाता है। वह कोई भी व्यक्ति आप्त हो सकता है जो यथार्थरूप में ज्ञात पदार्थ को उसी रूप में व्यक्त करने की इच्छा से वाक्य प्रयोग कर रहा हो।

न्याय में शाब्दबोध-

नैयायिकों के अनुसार शाब्दबोध स्थल में 'पदज्ञान' करण है क्योंकि पदों को सुनकर ही शाब्दबोध होता है किन्तु केवल पदों को सुन लेने मात्र से शाब्दबोध न हो सकेगा। श्रोता को **पदार्थस्मरण** भी आवश्यक है अर्थात् पदों के अर्थों का स्मरण हुये बिना शाब्दबोध न होगा। पदार्थस्मरण के लिये आवश्यक है कि श्रोता को शब्द एवं अर्थ के बीच वाच्यवाचकभाव सम्बन्ध का ज्ञान हो-शक्ति ज्ञान हो- यह ज्ञान हो कि शब्द की शक्ति अमुक अर्थ में है। 'गो' शब्द की शक्ति सास्नालांगूलचतुष्पदविशेष में है अर्थात् 'गो' शब्द एतज्जातीय पशुविशेष को कहते हैं। तभी श्रोता 'गौ' पद को सुनकर 'गौ' अर्थ का स्मरण कर सकेगा। इस प्रकार **शक्तिज्ञान** को पदार्थस्मरण में सहकारी माना गया है[2]।

शक्तिः - पदेन सह पदार्थस्य सम्बन्धः

पद का पदार्थ के साथ सम्बन्ध शक्ति कहलाता है। 'इस शब्द से यह अर्थ समझा जाए' इस प्रकार का संकेत ही शक्ति कहलाता है[3]।

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* शोधच्छात्र, संस्कृत विभाग, दिल्ली विश्वविद्यालय, नई दिल्ली abhayoct22@gmail.com

[1] शब्दोऽम्बरगुणः (प्रशस्तपादभाष्य-शब्दप्रकरण)

[2] शक्तिधीः सहकारिणी। (न्यायसिद्धान्त मुक्तावली)

[3] अस्माच्छब्दादयमर्थो बोद्धव्यः।

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Organic & Supramolecular Chemistry

Efficient Reversible Optical Sensing of Water Achieved through the Conversion of H-Aggregates of a Merocyanine Salt to J-Aggregates

Priya Ranjan Sahoo, Kunal Prakash, Ajeet Kumar, and Satish Kumar*[a]

Dedicated to a colleague Late Mr. K. M. Mathew

A stable MC (merocyanine)-spiropyran as *p*-toluenesulfonate salt was synthesized. The structure of the merocyanine salt form of the spiropyran was established by using IR, ^{1}H-NMR, ^{13}C-NMR, 2D-NMR and HR-MS spectroscopic techniques. The MC salt was employed as an optical probe for the detection of trace water content in the organic media using the naked eye, UV-Visible and fluorescence spectroscopic techniques. The DLS and TEM measurements were used to support the aggregation and disaggregation of the MC salt form. The results established the conversion of H- aggregates to J- aggregates can be used for the efficient detection of trace water content in organic media. The optical probe was further used to sense and quantify water molecules associated with the metal salts. The probe can be used multiple times for sensing water. The results provide insightful opportunities for practical applications of sensing trace water content in organic solvents and coordinated to metal ions.

Introduction

The stimuli-responsive assembly and disassembly process is being extensively investigated to understand and mimic biological functions.[1] Stimuli-responsive assemblies, in general, can be constructed using small monomer units through intriguing non-covalent interactions to achieve pH, temperature, light or solvent composition responsive systems.[2] The stimuli-responsive assembled structures are also appreciated for potential applications in areas such as drug delivery and sensing.[3] Among a variety of stimuli-responsive molecules, merocyanine dyes are known to form H- or J-aggregates through either face to face stacking or end to end stacking interactions.[4] Both H- and J-aggregates can be distinguished using absorption or emission spectroscopy. The formation of aggregates, shift the absorption band towards higher energy (H-aggregate) or lower energy (J-aggregate).[4] In response to aggregation, the fluorescence spectra in general displays an intensity enhancement (J- aggregate) or quenching (H-aggregate).[4] Aggregation of merocyanine dyes can be induced through external stimuli or change in temperature or light exposure or addition of an ion or molecule.[5] If the change in aggregation state is brought through the addition of an analyte, the change in spectral properties can be used for quantification and detection of an analyte. In this context, mapping out molecular receptors that can detect and quantify water is enormously important due to the harmful impact of water in a variety of processes in the laboratory and industry.[6] The presence of water in the organic solvents affect the electronic micro/nano devices and chemical productions in the industrial sector.[7] The industrial processes in pharmaceutical, petrochemical, paper and food processing industry are also severely affected by the presence of water as an impurity.[8] The presence of water in some chemical reactions often results in the low yield of the product or the reaction ceases.[6] The problem is critical, when dealing with organometallic reagents due to their extremely fast reaction with water, causing fires and explosions.[9] The presence of water in the petroleum products causes severe damage to the engines and leads to failure, particularly at low temperature due to clogging of fuel ducts.[6]

The commonly used methods for sensing water include Karl Fischer titration, chromatography, electrochemical and electrophysical methods.[10] However, such systems suffer from challenges like portability, precision, electromagnetic interferences and safety due to the use of electromagnetic radiation.[6,10b, 11] Therefore, there is a need to develop, faster, and easy to use portable water sensing systems with optical signals. The sensors with the optical response and high sensitivity are well suited for this purpose in comparison to electrochemical or electrophysical methods using electrodes[12] or other means,[13] as they are simple and convenient to use under laboratory and industrial conditions.[6,14] Although, colorimetric

[a] P. R. Sahoo, K. Prakash, A. Kumar, Dr. S. Kumar
Department of Chemistry
St. Stephen's College
University Enclave
Delhi-110007
E-mail: satish@ststephens.edu

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ORIGINAL RESEARCH ARTICLE

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Alginate based nanoparticles as a carrier matrix for the delivery of calixarene derivative as Pharmaceutical compound (Funded Work)

ABHISHEK SAXENA, NEETA BHAGAT, 2SATISH KUMAR, LOVNISH SIYAL, BENU KUMAR AND RACHANA SAHNEY

DOI: http://dx.doi.org/10.22376/ijpbs.2017.8.3.p217-224

Abstract:

Modern medicines are in urgent need of hyphenating new therapeutics, which can act as antimicrobial agent. Calixarenes are versatile macromolecules which can serve as a platform for the design and development of biologically active therapeutics. But the presence of aromatic ring structure in the calixarenes skeleton renders it hydrophobic which requires a hydrophilic carrier to reach the target cell efficiently for drug action. The present work is a comparative study of antimicrobial activity of sodium salt of p-sulfonato-calix-4-arene (calixarene derivative) in aqueous solution (phosphate buffer saline) and encapsulated in hydrophilic nanocarrier – alginate nanogel cross-linked with Ca^{+2}/Ba^{+2}. The alginate nanogels were characterized with respect to their size, encapsulation efficiency and their drug release profiles. Antimicrobial activity of p-sulfonato-calix-4-arene and alginate nanogels loaded with the p-sulfonato-calix-4-arene was determined by disc diffusion method and colony forming unit (CFU) method against drug resistant strain of *Escherichia coli* (MTCC 443). The experimental results suggest that the encapsulated calixarene derivative in hydrophilic calcium alginate nanogels is potentially best candidate against *E.coli* strain at much lower concentration than the free calixarene derivative soluble in phosphate buffer saline (PBS).

Keywords: Alginate nanogels; Drug Delivery; Hydrophilic carrier; Calixarene derivatives

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A fast, highly selective and sensitive anion probe stemmed from anthracene-oxazine conjugation with CN^- induced FRET

Kunal Prakash, Priya Ranjan Sahoo, Satish Kumar*

Department of Chemistry, St. Stephen's College, University Enclave, Delhi, 110007, India

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ABSTRACT

An anthracene-oxazine conjugate was synthesized by hybridizing the fluorescent anthracene unit with the photochromic nitrosubstituted oxazine. The structure of the conjugate was established by using IR, NMR, HR-MS and single crystal X-ray crystallography. The anthracene-oxazine conjugate was evaluated for affinity towards different anions in aqueous medium and selectivity towards cyanide ion was observed through development of color visible to the naked eye as well as through changes in fluorescence signal. An excellent value of 58 nm limit of detection value was obtained, which indicated an excellent sensitivity of the probe towards cyanide ion. The probe displayed fluorescence quenching via intramolecular energy transfer from the hybridized anthracene unit to the parent oxazine photochrome upon addition of the cyanide ions in aqueous medium. DFT calculations were performed to support the experimental data.

1. Introduction

Adaptive photo responsive molecules that emulate environmental and biological systems have taken a huge leap forward [1,2]. The potential applications of the photoresponsive systems in the field of toxic ion recognition are emerging in the area of supramolecular systems [3]. For instance, photochromic hybrid probes are promising candidates due to reversible performance displayed via external stimulation [4]. Mimicking the function of hybrid probe towards obvious color change is of particular interest. Besides that, photochromic oxazines are studied enormously due to their fast switching tendency and find applications in photoelectric conversion and light controlled ion detection [4,5]. Earlier, these have been investigated for sensing cyanide ion by *Raymo and co-workers* [6]. The existence of photocleavable C_{spiro}-O linkage produces two interconvertible isomeric forms of photochromic molecules with the help of light (UV and visible). Out of closed (OX) and open forms (IN), stability of the open form depends on the substituents present on the system. The structure of IN form normally produces a partial positive charge on the nitrogen atom, which ultimately reduces the electron density at the C_{spiro} carbon atom by intramolecular delocalization of electron density through a two way double bonded track. The open form with a slight positive charge can attract anionic species such as CN^- into its cavity. Studies have indicated that the cyanide ion is an extremely toxic substance polluting our environment [7]. This well-known byproduct of the chemical industry, leaves behind a greater risk to the surrounding habitats [8]. The United States Environmental Protection Agency (USEPA) [9,10] has set a maximum tolerable limit of CN^- at 7.8 μM, while the WHO [11] has set a limit of 1.9 μM [12]. Cyanide pollution caused by rampant industrialization has had a direct impact on environment and is among the well-recognized factors of its misery [13]. The ill effects of cyanide pollution have disastrous consequences which ultimately choke the human masses [11]. Lots of efforts have been utilized in the recent past to tailor specific host molecules for cyanide trapping. Meanwhile, more effective measures such as design of potential probes are necessary to make low-cyanide transitions in development right away. Among the available chemosensors, naked eye colorimetric sensors for toxic anions have received special attention [14,15]. However, the sensor performance is known to be affected by the interference from other anions such as acetate or fluoride [16,17]. Therefore, photochromic molecules which are known to bind cyanide ion through covalent linkages and produce distinct visible color change are viable alternative for cyanide recognition [18]. The colored form of the photochromic molecule is known to possess a partial positive charge, which can attract polar and negatively charged anions. The color change induced by anions in dark can be used to confirm the presence of

* Corresponding author.
E-mail address: satish@ststephens.edu (S. Kumar).

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DELHI-110007

ST. STEPHEN'S COLLEGE DELHI

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Organic & Supramolecular Chemistry

Visible Light Controlled Aggregation of a Spiropyran-HSO_4^- Complex as a Strategy for Reversible Detection in Water

Ajeet Kumar, Kunal Prakash, Priya Ranjan Sahoo, and Satish Kumar*[a]

Dedicated to Mr. K. M. Mathew (Former bursar, St. Stephen's College)

A merocyanine salt form of a substituted spiropyran was synthesized and evaluated for stimuli-responsive properties. The HSO_4^- induced H-aggregation of the merocyanine salt was used as a strategy for detection in pure water. The anion induced aggregation was controlled by light, which converted the open merocyanine form into the closed spiropyran form. The formation of the closed form released the hydrogen sulfate ion. The DLS and TEM analyses were used to investigate the aggregation and disaggregation of the merocyanine salt form of a spiropyran. Therefore, the study establishes the first example of reversible, highly selective and nanomolar level response towards HSO_4^- ion in water.

Introduction

The reversible control of supramolecular assembling and the disassembling process can play a vital role in simulating the biological functions such as conversion of microtubules and tubulin dimer.[1] Different types of stimuli such as light,[2] pH,[3] temperature,[4] solvent composition[5] and specific guest can be used to control the assembling and disassembling process. This approach was investigated intensively to design and develop interesting, well-defined molecular assemblies with diverse properties for applications in various areas of chemistry and biology.[6] The non-covalent interactions between host and guest are the main driving force for the reversible formation of supramolecular host assemblies.[7] Such interaction can be fine-tuned with appropriate guest species or substituent to get an appropriate optical signal. The J- and H- aggregates of organic dyes are also well-known examples of supramolecular assemblies with the optical response, which were utilized to develop chemosensors with an optical response.[7] The H-aggregates are known to produce hypsochromically shifted absorption band, while J-aggregates produce bathochromically shifted absorption band. The formation of J-aggregates displays an increase in fluorescence intensity, while H-aggregates generally display a fluorescence quenching response.[7–8] However, examples are available in the literature, where H-aggregates display an increase in fluorescence intensity.[7,9] A variety of sensors based on J-aggregates are used to develop colorimetric and fluorometric sensors, but rarely H-aggregates are used for similar applications.[7–8,10] However, interconversion between H- and J-aggregates was rarely utilized to develop a sensor for an analyte.[11] The sensing device with good optical response (colorimetric and fluorometric) for the detection and monitoring of toxic anions is appealing due to the convenient processing such as simple naked eye detection technique in comparison to other expensive techniques.[12] The sensing devices for a superior response can be fine-tuned with suitable functionalities with an aim towards improved optical response.[13] The HSO_4^- ion plays a significant role in biological and environmental processes.[14] Generation of toxic sulfate ions, on dissociation at high pH value, pose serious implications on human health and the toxicity causes serious issues and creates dysfunctions like respiratory paralysis, skin irritation etc.[15] The enhanced role of HSO_4^- in radioactive waste management,[16] medical diagnosis provides a driving force for the development of a selective sensor for remedial measures.[17] Increased level of HSO_4^- seems toxic to the natural habitat due to potential side effect leading to acid rain.[18] Therefore, there is a need to develop sensing system to counterbalance the harmful effects of HSO_4^-. The detection of HSO_4^- is more challenging and less explored owing to its amphiphilic character as well as the complex mode of action.[15] The reported receptors for HSO_4^- are either active in a fully organic solvent[16] or in a semi-aqueous solvent.[14,17] The challenge multiplies while dealing with real-time monitoring of analytes in pure water or without any organic co-solvent. The literature survey revealed only a few selective HSO_4^- sensor in pure water.[19] The other examples include indolinium dyes,[7] azo dyes,[20] quinoline based receptors,[21] metal-organic complex,[22] BODIPY based receptor[23] and adamantane-dipyrromethane conjugate.[24] In this context, spiropyran is also used to

[a] A. Kumar, K. Prakash, P. R. Sahoo, Dr. S. Kumar
Department of Chemistry
University Enclave, St. Stephen's College
Delhi-110007, India

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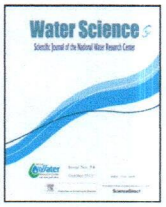

Research Article

Adsorption of heavy metals from wastewater using agricultural–industrial wastes as biosorbents

Abhishek Saxena [a], Manish Bhardwaj [a], Tanu Allen [a], Satish Kumar [b], Rachana Sahney [a,*]

[a] *Amity Institute of Biotechnology, AUUP, Noida 201313, India*
[b] *St. Stephen's College, University of Delhi, New Delhi 110007, India*

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1. Introduction

The contamination of the natural environment by heavy metal is an emerging problem in the world. Remediation of these contaminants from our environment is posing a technological challenge for us. According to the European Union's Restriction of Hazardous Substances (RoHS) Directive, application of lead, cadmium, and mercury in the manufacturing of electrical and electronic equipment are banned as they impart a hazardous effect on our health (European Parliament, 2002). These metal pollutants accumulate in the environment due to their non-biodegradable nature resulting in the contamination of food and water (Vries et al., 2007). Therefore, only permissible limits of these metal toxicants defined by World Health Organization (WHO, 2008) are strictly allowed in the drinking water. Some heavy metals like nickel and lead are purely toxic and are frequently found in industrial wastewater. The permissible values for Ni in serum is 0.2 μg/L and in urine is 1–3 μg/L for a healthy adult, as defined by Agency for Toxic Substances and Disease Registry (ATSDR) of United States (ASTDR, 2005). The most adverse health effect associated with Ni exposure is dermatitis which occurs through dermal contact with Ni. Conventional methods employed for heavy metal remediation are solvent extraction, precipitation, coagulation, reverse osmosis, adsorption, chemical oxidation and reduction, electro-dialysis and ion-exchange (Meunier et al., 2006; Djedidi et al., 2009; Kurniawan et al., 2006; Lee et al., 2006) But at metal ion concentration of 100 ppm or less, these are costly and ineffective too (Inbaraj et al., 2009). Bioremediation is a newer approach for the eradication of these heavy metals (Gaur et al., 2014) in which the removal of metal toxicants employ application enzymes, microorganisms, and plants which are eco-friendly in nature. It is one of the most favourable methods as it offers better results by utilizing low-cost materials in comparison to the conventional expensive means. A large number of literature studies indicate that the bioremediation of heavy metal

* Corresponding author.
E-mail addresses: asaxena4@amity.edu (A. Saxena), manishbhardwaj1274@gmail.com (M. Bhardwaj), tallen@amity.edu (T. Allen), Satish64@gmail.com (S. Kumar), rsahney@amity.edu (R. Sahney).

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Review

Light controlled receptors for heavy metal ions

Priya Ranjan Sahoo, Kunal Prakash, Satish Kumar*

Department of Chemistry, St. Stephen's College, University Enclave, Delhi 110007, India

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ABSTRACT

This review focuses on the recent growth in the photo triggered molecular receptors for heavy metal ions. The photochromic unit in such molecular receptors performs as a trigger unit to allow control over a range of the properties through an external stimulus. This review opens up with the new opportunities for the development of host molecular motifs for heavy metal ion sensing applications. The photochromic switches based on a chemical structure like spiropyran, chromenes and spirooxazines tagged with appropriate chromogenic or fluorogenic unit reported till date have been summarized and categorized by the selectivity of metal ion to achieve the suitable optical response. The review has relevance for designing new photoreversible switches with the interesting optical response for environmentally important heavy metal ions.

Contents

* Corresponding author.
E-mail address: satish@ststephens.edu (S. Kumar).

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