

3.71. Number of functional MoUs /linkage with institutions/ industries in India and abroad for internship, on-the-job training, project work, student / faculty exchange and collaborative research during the last five years

S.No.	Name of the organization with whom MOU/Collaboration being signed	Purpose of MOU/Collaboration
1	Department of Chemical Engineering and Materials Science, University of Minnesota Twin Cities, 421 Washington Avenue, Minneapolis, Minnesota 55455, United States.	Collaborative Research
2	Irving Medical Centre, Columbia University, New York, United States.	Collaborative Research
3	Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08854, USA.	Collaborative Research
4	Organic Semiconductor Centre, SUPA, School of Physics and Astronomy, University of St Andrews, North Haugh, St Andrews, Fife KY16 9SS, U.K.	Collaborative Research
5	Department of Mechanical & Construction Engineering, Faculty of Engineering and Environment, Northumbria University, Newcastle upon Tyne, NE1 8ST, UK	Collaborative Research
6	Computational and Bio Simulation Research Group, University of Calabar, Nigeria	Collaborative Research
7	Green Chemistry & Materials Modelling Laboratory, Department of Chemistry, Khalifa University of Science and Technology, P.O. Box 127788, Abu Dhabi, United Arab Emirates	Collaborative Research
8	Chemical Crystallography Laboratory, Khalifa University of Science and Technology, P.O. Box 127788, Abu Dhabi, United Arab Emirates	Collaborative Research
9	Green Chemistry & Materials Modelling Laboratory, Department of Chemistry, Khalifa University of Science and Technology, P.O. Box 127788, Abu Dhabi, United Arab Emirates	Collaborative Research
10	Natural Product Chemistry and Process Development Division, CSIR-Institute of Himalayan Bioresource Technology, Palampur, Himachal Pradesh, India	Collaborative Research
11	CSIR-Medicinal Chemistry Division, I ndian Institute of Integrative Medicine, Sanatnagar, Srinagar 190005, J&K, India.	Collaborative Research
12	Indian Institute of Technology Kharagpur, Kharagpur-721302, West Bengal, India.	Collaborative Research

13	Department of Pharmaceutical Chemistry, Progressive Education Society's Modern College of Pharmacy, Pune, India.	Collaborative Research
14	National Institute of Technology, Hazrotbal, Srinagar 190006, J&K, India	Collaborative Research
15	IIT Delhi	Collaborative Research
16	IISER Pune	Collaborative Research
17	NIT Srinagar	Collaborative Research
18	IIT Delhi	Collaborative Research
19	Raja Ramanna Centre for Advanced Technology Indore	Collaborative Research
20	Dr. B. R. Ambedkar Center for Biomedical Research, University of Delhi, New Delhi, India	Collaborative Research
21	IIIM Srinagar, Sanatnagar	Collaborative Research
22	School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded 431606, India	Collaborative Research
23	Department of Chemistry and Earth Sciences, Qatar University, Doha 2713, Qatar	Collaborative Research
24	Organic and Supramolecular Functional Materials Research Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi	Collaborative Research
25	Chemical and Biochemical Engineering Department, Indian Institute of Technology Patna, Bihta, Patna, 801106, Bihar India	Collaborative Research
26	R&D Centre, Laurus Laboratories Limited, DS-1, IKP Knowledge Park, Genome Valley, Turkapally, Shameerpet, Hyderabad, 500078, Telangana India	Collaborative Research
27	Chemical and Biochemical Engineering Department, Indian Institute of Technology Patna, Bihta, Patna, 801106, Bihar India	Collaborative Research
28	Department of Chemistry, DAV University, Jalandhar 144012, Punjab, India	Collaborative Research

29	Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR) Jakkur, Bangalore 560046, India	Collaborative Research
30	Green Chemistry & Materials Modelling Laboratory, Department of Chemistry, Khalifa University of Science and Technology, P.O. Box 127788, Abu Dhabi, United Arab Emirates	Collaborative Research
31	Department of Physics, University of the Free State, Bloemfontein, ZA9300, South Africa.	Collaborative Research
32	Institut Charles Gerhardt Montpellier UMR 5253, CNRS, ENSCM, Univ.Montpellier, Montpellier, France.	Collaborative Research
33	Research Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba 305-0044, Ibaraki, Japan.	Collaborative Research
34	City University of Hong Kong Shenzhen Research Institute, Yuexing 1st Road, Shenzhen Hi-Tech Industrial Park, Nanshan District, Shenzhen, P. R. China.	Collaborative Research
35	Department of Physics, University of the Free State, Bloemfontein ZA9300, South Africa.	Collaborative Research
36	School of Chemistry, Trinity College Dublin, University of Dublin, Dublin 2, Ireland.	Collaborative Research
37	Department of Chemical, Biological & Macromolecular Sciences, S. N. Bose National Centre for Basic Sciences, Kolkata 700106, India.	Collaborative Research
38	Academy of Scientific and Industrial Research (AcSIR), Ghaziabad 201002, India; Natural Product & Medicinal Chemistry, CSIR-Indian Institute of Integrative Medicine, Jammu 180001, India.	Collaborative Research
39	Department of Chemistry, University of Jammu, Jammu, Jammu & Kashmir 180006, India.	Collaborative Research
40	Department of Chemistry, Savitribai Phule Pune University (formerly University of Pune), Ganeshkhind, Pune-411007, India.	Collaborative Research
41	Department of Chemistry, Central University Haryana, Mahendergarh 123031, India.	Collaborative Research

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Perspective

Pharmaceutical Cocrystals: A Perspective on Development and Scale-up of Solution Cocrystallization

Anindita Saha, Aadil A. Ahangar, Aijaz A. Dar,* <mark>Satyanarayana Thirunahari, and Jose V. Parambil*</mark>





III Metrics & More

ABSTRACT: Pharmaceutical cocrystals represent an emergent class of successful materials designed based on crystal engineering principles, in which the limitations of the extant drugs are addressed. Though the number of newly reported cocrystals is increasing exponentially, the scale-up of the cocrystallization process has not received enough attention. Solution cocrystallization techniques offer scalable processes that can utilize conventional crystallization machinery and process analytical technologies. The presence of multiple components and competing kinetics of the starting materials as well as the cocrystal make the cocrystallization process harder to study and control. This perspective emphasizes the importance of multicomponent phase



diagrams for identifying operating regions in solution cocrystallization and discusses the effects of various operating parameters on the process kinetics. It also covers the intermolecular interactions involved in cocrystal development, cocrystallization methods, and quality control in pharmaceuticals. Furthermore, the role of the Design of Experiment and Quality by Design in scaling up the cocrystallization process efficiently is highlighted. A systematic decision tree has been proposed for scaling up the production of promising cocrystals using solution-based techniques, which can effectively address the current challenges in large-scale cocrystal production and help bring these potential materials to the market in the near future.

INTRODUCTION

Crystal engineering utilizes the knowledge of crystal structures for developing materials with well-designed functionality by harnessing the potential of intermolecular interactions.¹ The conceptual origin of crystal engineering can be traced back to the time when Bragg attempted to generalize the crystal packing in polycyclic aromatic hydrocarbons, based on the similarities between the crystal structures of naphthalene and anthracene.², With the passage of time, the solid-state photochemical reactivity of trans-cinnamic acids and other alkenes by Schmidt and his group in 1950-60 laid the foundation of crystal engineering.⁴ Though it is also claimed that the term crystal engineering was coined by him, it is commonly accepted that the term was coined by Pepinsky in 1955.⁵ Since then, the discipline remained open to scientific curiosity, and several important topics in solid-state including phase transition, gas-solid reactions, crystal polarity, and polymorphism were included in the spectrum of crystal engineering.⁶⁻¹³ Focused efforts in the area came from the work of Ermer's study of the crystal structure of adamantane-1,3,5,7-tetracarboxylic acids,¹⁶ and Robson's study on the interpenetration of the crystal structure of coordination compounds.¹⁷ Desiraju's and Gavezzotti's work in the early 1990s¹⁸ further defined the area and additional efforts from Robertson and Dunitz involving understanding of the transformation of a molecule to crystal established it

further.^{19,20} Later on, Desiraju identified three important parameters of the area as (i) study of intermolecular interactions, (ii) study of packing modes, and (iii) study of crystal properties.²¹ An important development in the area was the inclusion of cocrystals. Though a cocrystal was first reported in 1783, the design directional work has only been reported after 1963, since Etter defined the hydrogen bonding rules.^{22–24} Cocrystals are defined as "solids that are crystalline single-phase materials composed of two or more different molecular and/or ionic compounds generally in a stoichiometric ratio which are neither solvates nor simple salts."²⁵

Recently, pharmaceutical cocrystals, with at least one active pharmaceutical ingredient (API) component, have emerged as a highlight achievement of crystal engineering.^{26–28} Nearly 90% of small drug molecules are already investigated or are at advanced levels of investigation in studies, and nearly 40% of the commercial drugs suffer from serious solubility limitations. An

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Molecular salts of the isoniazid derivatives. Expanding the scope of sulfonate-pyridinium synthon to design materials



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ABSTRACT

Understanding the intermolecular interactions is central to crystal engineering and is pivotal in designing of the new materials. Of recent we have reported sulfonate-pyridinium interaction as robust synthon and herein we utilize the interaction to develop molecular complexes: [(ISN-I3C-H)⁺(5-SSA-H)⁻] (1), [(ISN-pV-H)⁺(5-SSA-H)⁻] (1), H)⁻.MeOH·H₂O] (2), and [(ISN-oV-H)⁺(5-SSA-H)⁻.H₂O] (3). 1–3 have been obtained by reaction of isoniazid derivatives: ((1H-indol-3-yl)methylene)isonicotinohydrazide (ISN-I3C), isonicotinic acid (4-hydroxy-3-methoxybenzylidene)-hydrazide (ISN-pV) and isonicotinic acid (2-hydroxy-3-methoxy-benzylidene)-hydrazide (ISN-oV) with 5-sulfosalicylic acid (5-SSA-2H). Molecular salts 1 and 2 manifest direct charge assisted sulfonate-pyridinium interaction, while, in 3, the synthon is masked by lattice water. The Schiff base cations in 1 and 2 stack together through strong π -interactions forming 2-dimensional layers and 1-dimensional tapes, respectively, which, in turn, are bridged by the organo-sulfonate anions into a 3-dimensional ionic solids. While the crystal formers in 3, the hydrogen bonds are utilized to form three molecule thick sheets, which aggregate through C–H···O and π - π interactions to form a 3-dimensional supramolecule. Hirshfeld studies corroborate with structural studies and validate that reciprocal O-H/H-O interactions are the chief intermolecular interactions in these oxygen rich compounds while weak dispersive H-H contacts are the second dominant interactions responsible for the molecular packing. Framework energy, as well as individual contribution of columbic, potential and dispersive forces towards molecular packing, are visualized through framework energy analyses of 1-3, which also substantiate that very robust sulfonate-pyridinium contact is not the strongest intermolecular contact. The resultant multicomponent crystals exhibit enhanced optical properties, which are attributed to proton transfer and/or π -stacking interactions. The band gap values of 1-3 observed in the Tauc plots corroborate with charge transfer interactions. The products also exhibit enhanced solubility in methanol, higher than the isoniazid derivatives, and the thermal stability up to 240 °C. The molecular salts have also been screened for preliminary biological studies.

1. Introduction

Chemistry of the covalent and coordinate bonds has been pursued with great vigour since days of yore and together organic synthesis and coordination chemistry have led to significant advances in science and technology through the development of new drugs, materials, and devices [1–8]. Of recent chemistry of non-covalent interactions like hydrogen bond [9–12], ion- π [13], and π - π [14–16] interactions has been utilized to design the molecular assemblies and the seminal contributions of Desiraju [17] and Etter [18] have paved the way for the establishment for rational utilization of these non-covalent interactions under a

separate field of the supramolecular chemistry. Crystal engineering has been instrumental in understanding the extant and discovery of novice supramolecular interactions, as well as their utilization for the development of new materials [19]. It has also been influential in designing the bespoke multi-component crystals with enhanced mechanical [20], physicochemical [21] and pharmacokinetic properties [22,23]. Co-crystallization of the pharmaceuticals is a convenient alternative to organic synthesis to develop drugs and the approach has been successful to address the solubility limitation, toxicity and other physicochemical aspects of existing drug molecules [24]. At least three of the co-crystals with better efficiency are available in the market [25,26].

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Article

Physicochemical and Anti-fungal Studies of the Pharmaceutical Cocrystal/Salt of Fluconazole

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synthesis that can be used to manipulate molecular behavior promptly and economically. We report the preparation and characterization of the pharmaceutical organic salt (FLC-C) of fluconazole (FLC) and organo-sulfonate (NDSA-2H), based on the sulfonate-pyridinium supramolecular synthon. Structural studies validate the crystallization of the two-component stoichiometric crystal with two molecules of water in the triclinic $P\overline{1}$ space group. The anticipated proton transfer between the crystal forms leads to ionic interactions, augmenting the organic salt's thermal stability. Hirshfeld studies of FLC-C help to understand the role and significance of different types of intermolecular interactions responsible for crystal packing. The structural and theoretical studies indicate the absence of $\pi-\pi$ interactions in FLC-C, which account for the incipience of solid-



state emission in the product. The solubility studies establish augmented aqueous solubility of FLC-C over pristine FLC at physiological pH values of 2 and 7. Interestingly, in in vitro studies, FLC-C appears to serve as a potential alternative to FLC, displaying a wide spectrum of antifungal activity. FLC-C is active against several human pathogenic yeast strains, including the leading and emerging *Candida* strains (*Candida albicans* and *Candida auris*, respectively), at comparable and/or lower drug concentrations without showing any enhanced host cell toxicity. Interestingly, the pharmaceutical co-crystal also displays fluorescence properties inside the *Candida* cells.

KEYWORDS: crystal engineering, hydrogen bond, drug modification, drug resistance, human pathogenic fungi, fluconazole

■ INTRODUCTION

Fungal infections represent one of the greatest health challenges, as around 1.7 million people suffer from fungal infections globally. Systemic infections caused by fungi that have penetrated and developed themselves in the deeper tissues are referred to as invasive fungal infections (IFIs) and can be fatal.^{1,2} IFIs are most frequently caused by Aspergillus, Cryptococcus, and Candida genus-associated species, which account for more than 90% of fungal-associated deaths.³⁻⁵ Unfortunately, the treatment options for fungal diseases are very limited due to the limited classes of antifungal drugs. These fungal species have acquired multiple antifungal drug tolerance mechanisms, like drug efflux pump overexpression, biofilm formation, etc.^{6,7} Moreover, because of the drawbacks of existing antifungal treatments, such as host cell toxicity, interactions, limited administration methods, etc., treatment of invasive fungal diseases is still a challenge. To lower the high mortality of invasive fungal disease and to control the development of resistance to conventional treatment strategies,

newer and/or modified antifungal treatments that are more effective are required.⁸ The development of novel antifungals is also important, as the drugs in the market are scarce and fail to provide complete security. Poor solubility of antifungals is yet another limitation, decreasing their bioavailability and scope of oral administration.^{9,10} Therefore, the current antifungal pipeline needs to be improved, and new or improved antifungals with a wide range of efficacy should be developed.¹¹ Though different approaches have been used over the years to find novel, promising antifungal leads, little success has been achieved.¹²

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Validation of the supramolecular synthon preference through DFT and physicochemical property investigations of pyridyl salts of organo-sulfonates[†]

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Synthon preference is perceived in the pyridyl salts of multi-functional organo-sulfonates and validated through density functional theory (DFT) studies. The salt 1 of 5-sulfosalicylic acid (5-SSA-3H) as well as previously reported pyridyl salts of 5-SSA-3H indicates preferential formation of sulfonate-pyridinium interaction I over common and robust carboxylic-pyridine/carboxylate-pyridinium II as well as hydroxylpyridine/hydroxylate-pyridinium III interactions. Pyridyl salts of further functional organo-sulfonates 8-hydroxyquinoline sulfonic acid (8-HQSA-2H) 2 and Schiff bases of sulfanilic acid and syringaldehyde (4-ABSA-SA-2H) 3 show preference for bifurcated hydroxyl assisted pyridinium-pyridine IV and methoxy assisted pyridinium-hydroxylate V synthons. The observed synthon preference is also supported by previously reported organic salts. The overall synthon preference IV \sim V > I \gg III \gg III is further validated through DFT studies, whereas QTAIM studies substantiate the electrostatic nature of interactions I-V with some covalent character. Hirshfeld studies of the organic salts indicate that reciprocal $O-H\cdots H-O$ and $H\cdots H$ interactions are the major interactions responsible for packing, whereas **3** exhibits higher C···C interactions than 1 and 2, which is substantiated by significant π -stacking in 3 and its absence in 1 and 2. Furthermore, the organic salts exhibit augmented thermal and chemical stability, plausibly due to the ionic nature of the crystal lattice. The optical behaviour of the salts corroborates with crystallographic packing and red shift in the absorption of **3** is attributed to $\pi - \pi$ interactions between crystal formers. Organic salts 2 and 3 exhibit augmented aqueous solubility compared to pristine precursors, and enhancement in the solubility of 3 is striking with a value of 1175% compared to the organosulfonate precursor.

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Introduction

Understanding of the intermolecular interaction and utilization of that understanding to design bespoke molecular solids defines crystal engineering.^{1,2} Robust intermolecular interactions have been identified and termed as supramolecular synthons by Desiraju.^{3–5} Intra-synthon competition and thermodynamic forces play a role in the crystallization process leading to quite a few possible stages of crystallization as reflected by Ostwald's law of stages⁶ and polymorphism.^{7,8} The presence of robust synthons

generally leads to the formation of kinetic products over close packed thermodynamic products. Being strong and reproducible, identification of the synthons enhances predictability of supramolecular synthesis. A prerequisite for rational supramolecular design, in addition to identification of synthons, is understanding the synthon hierarchy and transferability.9,10 Robust synthons have been documented;² however their hierarchy has not been well researched. Dunitz and Gavezzotti have reported cohesive energy calculations of some of the common but limited robust isolated synthon dimers using the PIXEL method, and it remains the only report where synthon hierarchy has been computed.¹⁰ Synthon transferability is a major challenge before crystal engineers to design and/or reproduce the supramolecular synthesis, and the process becomes even more challenging for multifunctional crystal formers. Hence, the exploration of synthon hierarchy, more particularly in the case of multifunctional systems, can be of enormous advantage to understand and design supramolecular synthesis. Such hierarchy of intermolecular interactions will be helpful to understand the phenomenon of synthon transferability,¹¹



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A high Z' structure of an organic salt with unusually high phase stability, nanoindentation, and mechano and vapo-fluorochromism[†]

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Understanding the molecular packing is pivotal to understand the process of crystal growth and the establishment of the structure-property relationship. We report a two-component organic crystal 1, with extraordinarily high Z = 64, Z'' = 32 and Z' = 16. Low Z' polymorphs of the reported structure remain elusive and crystallization and recrystallization from numerous solvent systems under different conditions yielded crystals with the same cell values. DSC and variable temperature powder-X-ray diffraction studies of the salt indicate the absence of any phase transition in the crystal prior to its melting point. The crystal exhibits unusually high thermal stability and does not undergo any phase transformation before melting, as validated by variable temperature powder X-ray diffraction and thermal studies. Quantification of the nanomechanical properties provides further structural insights. Interestingly, 1 exhibits rare dual stimuli-responsive behavior on grinding and exposure to base fumes.

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Introduction

Thermodynamics and kinetics compete during the crystallization of molecules. Thermodynamics encourages the close molecular packing while Ostwald's law of stages and the Curtin-Hammett principle forecast the formation of the kinetic products, during a crystallization process.^{1,2} Therefore, in a reaction vessel crystal formation is influenced by both thermodynamics and kinetics in a complex way.3 Z', defined as the number of symmetry-independent formula units in a crystal, represents yet another dimension to the crystal packing. Structures with Z' > 1 represent a meagre 8.8% while a paltry 0.01% of the reported structures represent $Z' > 4.^{4,5}$ High Z' structures represent unusual molecular arrangements which demand deeper analysis and investigation to understand the crystallization and crystal packing. The Durham University Z' Web Source⁶ and an exhaustive review by J. W. Steed⁷ on crystal packing problems provide a significant account of the importance of high Z' structures and an important discussion of factors leading to high Z' structures. A detailed review by Brock to classify high Z' structures also provides valuable insights into the topic, with conclusions like i) being very diverse, simple description of high Z' structures is not possible, ii) more than one factor can be responsible for the formation of a high Z' structure, and iii) some of the high Z' structures are stunningly complex to understand how they nucleate and grow.⁸

Very high Z' (presumed here for Z' > 12) structures, Table ESI-1,† are sparse and their statistical analyses remain inconclusive, e.g. molecular flexibility is ruled out as a reason while small rigid molecules are believed to pack as high Z' structures with higher frequency.9,10 However, of the six molecular salts based on flexible bis-pyridyl propane (BPP), reported by us recently, two packed with high Z' values, Table ESI-2.^{†11-15} This instigated us to further analyze the influence of the flexibility of the BPP crystal coformer on the crystal packing. Here, we conclude that the flexible BPP coformer packs into high Z' structures with a nearly equal probability of 8.75% as compared to an overall average of 8.8%, Table ESI-3.† However, an interesting offbeat statistic, in which there are 13.75% 4,4'-BPP cocrystal structures with at least two 4,4'-BPP molecules and 23.75% cocrystals with at least two molecules of either 4,4'-BPP or other crystal coformers in the asymmetric unit, further complicates the analyses.

Results and discussion

Based on our understanding of sulfonate-pyridinium supramolecular synthons,¹¹⁻¹⁶ an organic salt $[(4,4'-BPP-H)^+(4ABSA)^-]$ (1) with an unusual crystal structure was obtained. It crystallizes as colourless crystalline lumps from

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[‡] Ishtiyaq Ahmad and Arshid A. Ganie have contributed equally to the paper.



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Utility of Bis-4-pyridines as Supramolecular Linkers for 5-Sulfosalicylic Acid Centers: Structural and Optical Investigations

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Supporting Information



ABSTRACT: Supramolecular aggregation through a less explored {Ar-SO₃…H-py} synthon, formed by 5-sulfosalicylic acid (5-SSA-3H) and bis-4-pyridines viz. 1,2-di(4-pyridylethylene) (4,4'-BPE) and 4,4'-trimethylenedipyridine (4,4'-BPP), has been reported. Four molecular salts [(5-SSA-2H)⁻(4,4'-BPE-H)⁺·MeOH·2H₂O] (1), [(5-SSA-3H)(5-SSA-2H)⁻(4,4'-BPE-H)⁺· 2H₂O] (2), [(5-SSA-H)²⁻(4,4'-BPP-2H)²⁺] (3), and [(5-SSA-2H)₂⁻(4,4'-BPP-2H)⁺·2H₂O] (4) have been obtained by varying the flexibility and stoichiometry of the bis-4-pyridine linker. Two types of steplike chains formed by formers in 1 are associated by rare {(H₂O)₄(MeOH)₂} clusters into a three-dimensional (3-D) network. The lattice water molecule in 2 associates 5-SSA units into double layer chains that are further associated by a bis-4-pyridine linker into a 3-D supramolecular network. Four crystallographically different, one-dimensional chains in nonsolvated 3 are interwoven and held together by weak van der Waals forces. 4 forms a layered structure, and the layers are further aggregated through weak C-H…O interactions into a 3-D assembly. The UV-visible absorption and photoluminescence properties of these compounds have been examined in their solid state. Due to hydrogen and π - π bonding between the ligands and protonation of bis-4-pyridines, a remarkable red-shift of the absorption spectra has been observed. The photoluminescence properties examined for compound 4 show intense blue photoluminescence.

INTRODUCTION

Supramolecular chemistry has evolved as a major research area with diverse utility and immense potential.¹⁻¹⁰ A better understanding of supramolecular interactions and their association with crystal engineering over last two decades has resulted in the development of alternative solid forms with finely tuned properties.^{11,12} Supramolecular materials are emerging as applied materials in diverse fields, viz., sensing,^{13,14} molecular imaging,^{15–18} metal extraction,^{19,20} drug formulation and delivery,^{21,22} molecular machines,²³ and so on. Various attempts to utilize supramolecular building units, i.e., synthons to achieve rationality in design and establish structure-activity relationship (SAR), have been reported.²⁴⁻²⁶ With limited success, the quantitative structure activity relationship (QSAR) approach has also been employed to predict the formation of cocrystals.^{27,28} Furthermore, the knowledge deposited in the Cambridge Structural Database (CSD) is a useful tool for retrospective analysis, which can be utilized for the design and formulation of newer types of supramolecular aggregates.²⁹

However, a large ambivalence still exists in achieving the rational design of supramolecular assemblies, and the area demands further efforts to define more definitive approaches.

Bipyridyls are widely used ligands in coordination chemistry to achieve designer materials with fine-tuned structures.³⁰ Exobidentate ligands such as 4,4'-bipyridine (4,4'-BPY), its oxides, and longer analogues (named here as bis-4-pyridines) have been rationally employed to assemble discrete metal complexes into one-, two- and three-dimensional (1-D, 2-D, and 3-D) arrays with intriguing structures and applications.³¹⁻³³ These bis-4-pyridines have been adequately employed as supramolecular coformers as well.³⁴⁻⁴⁴ However, the attempts to employ them as designer coformers with rationality are limited and random. Tiekink and co-workers have reported cocrystals of 2,2'-dithiodibenzoic acid and

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Expanding the Scope of Hydroxyl-pyridine Supramolecular Synthon to Design Molecular Solids

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ABSTRACT: Supramolecular synthons, i.e., robust noncovalent interactions, are equivalents of the covalent bonds of organic synthesis in supramolecular chemistry. Exploring the novel synthons and further utilizing the extant ones are imperative to develop supramolecular chemistry further. Hydroxyl-pyridine, a neutral interaction, is a serendipitous but robust synthon observed in molecular complexes and cocrystals. Herein, we utilize this intermolecular interaction with a predesign for the development of new molecular complexes [(DHBA-2H)(4,4-BPY)] (1) and [(THBA-3H)(4,4-BPY).H₂O] (2), that have been further functionalized by the reaction with 4-iodo aniline to yield [4-I-DUIDA 2U)(4.4 DDY)] (2).



DHBA-2H)₂(4,4-BPY)] (3) and [(4-I-THBA-3H)(4,4-BPY)] (4). Molecular complexes 1 and 2 build upon a centrosymmetric $R_4^{4}(30)$ and non-centrosymmetric $R_6^{6}(32)$ synthons to form layered and reticular aggregates, respectively, which are stabilized by CH… π , CH…O, and $\pi - \pi$ contacts. The halogen interactions in the iodinated cocrystals 3 and 4 direct the supramolecular aggregation into zigzag and intriguing arc-interwoven three-dimensional solids, respectively. Cocrystals 1–4 provide an opportunity to investigate the influence of halogen atoms/bonding, on the execution of a hydroxyl-pyridine synthon. Incipience of color in cocrystals 1 and 2 and a remarkable color change in 3 and 4 are validated by diffuse reflectance (DR-Uv) studies. Interestingly, 3 exhibits irreversible thermochromism near its melting point which is also accompanied by emission turn-on. 1–4 show enhanced aqueous solubility via-a-vis an acid former, which is strikingly 17,943% for 3. Intermolecular interactions responsible for supramolecular aggregation are investigated in detail utilizing Hirshfeld, quantum theory of atoms in molecules (QTAIM), and noncovalent interaction index (NCI) analyses. The structural, physicochemical, and computational studies are compared to understand the structure–property relationship.

■ INTRODUCTION

Crystal engineering is a recent stratagem for developing functional materials with bespoke properties.¹⁻⁴ Supramolecular contacts are weak and often reversible and provide a convenient, economical, and progressivist alternative to organic and inorganic synthesis.5-7 The consequent supramolecular assemblies exhibit improvisation in their physicochemical⁸⁻¹⁰ and pharmacokinetic properties¹⁰⁻¹² and have found utility across the spectrum viz. organic light-emitting diodes,^{13,14} electronics,^{15,16} detectors,¹⁷ sensors,^{18–20} devices,²¹ molecular machines,^{22,23} catalysts,²⁴ drugs,^{25–27} etc. Robust supramolecular synthons first documented by Desiraju²⁸ are instrumental in developing new molecular solids and play the same role in supramolecular synthesis that a covalent bond plays in organic synthesis. Defined as structural units within supermolecules that can be formed and/or assembled by known or conceivable synthetic operations involving intermolecular interactions, synthons are central to crystal engineering. It is imperative to identify novel ones and further investigate the extant robust supramolecular synthons.²⁹

Supramolecular synthesis is an evolving subject, and some of the accompanying challenges include synthon reproducibility and reliability, synthon competition in multifunctional precursors in a reaction vial, synthon success rate, and synthon stability in polar media. Furthermore, postsynthetic modification in organic cocrystals is not well reported and can open up more opportunities.

Carboxylic acid-pyridine, carboxylic acid-amide, and hydroxyl-pyridine synthons are commonly observed in multicomponent crystals,³⁰ and the Cambridge structure database reports >90% occurrence of hydroxyl-pyridine interactions in the absence of strong hydrogen-bonding functionality.³¹

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Article

Hetero-Aggregation-Induced Tunable Emission in Multicomponent Crystals

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Article Recommendations

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ABSTRACT: Crystal engineering is a green and convenient approach to designing desirable materials through rational manipulation of intermolecular interactions. We have reported the lesser reported sulfonate—pyridinium intermolecular interaction for the design and synthesis of organic co-crystals with improved features. Here in we report the utilization of the interaction to tune the solid-state luminescence of organic precursor naphthalene disulfonic acid (NDSA-2H). Organic salts of NDSA-2H are synthesized and characterized with three isostructural bipyridyl co-formers: 4-phenylpyridine (4-PhPy), 2-phenylpyridine (2-PhPy) and 2,2'-bipyridine (2,2-bpy). Structural investigation validates aggregation of organic acid and base co-formers through sulfonate—pyridinium synthon and proton

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transfer between them. Compared to NDSA-2H, the molecular salts $[(4-PhPy-H)_2^+(NDSA)^{2-}\cdot 2H_2O]$ (1) and $[(2,2-BPY-2H)_2^+(NDSA)^{2-}]$ (3) undergo a blue and red shift, respectively, while solid-state emission of $[(2-PhPy-H)^{2+}(NDSA)^{2-}]$ (2) remains unaltered. This solid-state emission tuning is attributed to the different modes of crystal packing and arises from monomer emissions in 1 and 2 and excimer emission in 3. 3 also exhibits a relatively longer lifetime of 20.7 ns while 2 exhibits better quantum yields ($\phi = 22.7$). Solution-phase photophysical behavior has been investigated for representative co-crystal system 3, after validation of its solution-phase integrity. 3 undergoes a hetero-aggregation-induced tunable emission (HAITE) phenomenon in the water-acetone system to exhibit maximum emission intensity at 90% volume fraction of acetone, which is further validated by the diffuse light scattering (DLS) and scanning electron microscopy (SEM) studies. 3 also exhibits solvatochromism in terms of emission intensity change with the nature of the solvent, being brightest in methanol ($\phi = 29.3$) and very dim in water ($\phi = 10.1$).

■ INTRODUCTION

Crystal engineering is a fascinating approach to design materials with desired physicochemical properties for practical utility. It essentially involves understanding and utilization of weak and reversible noncovalent intermolecular interactions.^{1–5} Organic crystal engineering primarily focuses on the design and development of co-crystals, which represent an emergent class of functional materials. The co-crystal approach is a green alternative of organic synthesis^{6–9} and the co-crystal materials are emerging as alternatives for inorganic applied materials like semiconductors,¹⁰ nonlinear optics,¹¹ organic light-emitting transistors (OLEDs),¹² organic field-effect transistors,^{13–15} optical waveguides,^{16–19} sensors,^{20–23} and room temperature phosphors,²⁴ besides the pharmaceutical co-crystals.^{25,26} Unlike covalent bonds in organic molecules, the weak noncovalent interactions in crystal forms are reversible, malleable and elastic; hence, the physicochemical character-

istics of these systems may respond to different external factors.^{27,28}

Luminescent organic materials are important for their scope in their photoelectronic, 2^{29-31} optoelectronic³² and memory based applications.^{33,34} Construction and tuning of the emission in solid organics is challenging but important to achieve multicolor emission for the development of a new generation of applied materials. The serious challenge in the development of solid-state organic fluorochromic materials is aggregation caused quenching (ACQ), and achievement of multicolor emission tuning is still in infancy.

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Article

Polymorphism Steered Thermochromism in a Sulfonamide

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ABSTRACT: Color polymorphism is a rare but intriguing phenomenon, crucial for fundamental understanding and with broad implications for a number of industries. We report the facile preparation of six color polymorphs (forms I-VI) of a sulfonamide. All forms have been structurally characterized, and the studies attribute the color polymorphism to molecular rotations about the C=N-C-C dihedral (torsion 1). A definite correlation between color wavelength and value of torsion 1 has been established, indicating the tendency of red-shift with a decrease in values of torsion 1. Remarkable reversible (four forms) and irreversible (two forms) thermochromism arises due to controlled small and large angle



molecular rotations, respectively. Conformational energy scans suggest that the six polymorphs are located in one of two energy basins. Computational crystal structure prediction (CSP) was performed, taking into account the molecular flexibility to correctly locate all polymorphs on the crystal form landscape. The temperature-induced enantiotropic phase transition between III and IV was rationalized using free energy calculations within the harmonic approximation. Overall, this work reports a record six crystal polymorphs of a simple molecular compound with striking chromism and thermochromic behavior and emphasizes the importance of a joint experimental and computational approach to understanding and controlling polymorphism in conformationally flexible organic molecules.

KEYWORDS: Crystal engineering, Polymorphism, Thermochromism, Smart materials, Crystal structure prediction, Energy landscape

INTRODUCTION

Polymorphism is the ability of a molecule to exist in multiple crystal forms due to intramolecular flexibility (conformational polymorphism)¹ or intermolecular packing variations (packing polymorphism),² triggered by experimental conditions and process methods.^{3–6} Different polymorphs exhibit different properties and like allotropes and isomers, the polymorph behavior can vary leading to significant modulations in the physicochemical properties of supramolecular aggregates, and by extension, to new material and biomedical applications.^{7–9} Within the context of structural elucidation, polymorphs also provide a unique opportunity to establish structure–property relationships in materials.^{10,11}

Color is an important observable property to differentiate between the polymorphs; however, color polymorphism resulting from the variation in intramolecular twisting or packing is a rare phenomenon.¹² Color polymorphs present significant scope for advanced applications and can be used as temperature sensors, photoelectronic devices with multiplex capabilities, memristors, electroluminescent OLED materials, and micromechanical actuators.^{13–17} The phenomenon was first reported by Gattermann in 1885 with the identification of white and yellow crystalline forms of N-(4-methyl-2nitrophenyl)acetamide.¹⁸ Almost a century later, a third polymorph of this compound with an amber color was identified.¹⁹ Through structural elucidation of the three forms, it can be established that yellow and amber forms are packing polymorphs, while the white form is their conformational polymorph.^{20,21} Similarly, white, yellow and light-yellow forms of dimethyl 2,5-dichloro-3,6-dihydroxyterephthalate exhibit color polymorphism due to the difference in torsion angles and intermolecular contacts, as established through their structure analyses.^{22,23} 5-methyl-2-((2-nitrophenyl)amino)-thiophene-3-carbonitrile (ROY), however, is the most widely cited example of conformational color polymorphism, with 11 known polymorphs of which nine have been structurally characterized.^{24,25} Multiple structural analogues of ROY with mild substitutions²⁶ have also been reported to exhibit facile color polymorphism as the intramolecular hydrogen bond locks one of the two single bonds connecting aromatic rings and allowing the rotations about the other.²⁷

Extensive studies to understand color polymorphism in ROY, attributed color variations to the intramolecular twist: for planar molecular geometry with torsion angle (θ) values below 35°, the color is red, while for θ values between 45 and 58° and 65–76°, the color is in the orange and yellow range, respectively.²⁸ The observed decrease in the color wavelength corroborates with the decreased conjugation within the

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PDFelement

Broad Spectrum Tunable Photoluminescent Material Based on Cascade Fluorescence Resonance Energy Transfer between Three Fluorophores Encapsulated within the Self-Assembled Surfactant **Systems**

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Supporting Information

ABSTRACT: A broad spectrum tunable photoluminescent material with dual encryption based on a two-step fluorescence resonance energy transfer (FRET) between pyrene (Py), coumarin 480 (Cou480), and rhodamine 6G (R6G) in micelles of SDS and bmimDS is presented. The phenomenon is achievable due to the encapsulation of the fluorophores within these micelles. The transfer of energy as FRET between the pair Py and Cou480 showed ON at 336 nm and OFF at 402 nm in contrast to the FRET observed between the pair Cou480 and R6G that showed ON at 402 nm and OFF at 336 nm. However, the transfer of energy as FRET occurs from Py to R6G in the presence of Cou480 when excited at 336 nm, thereby making it a chain of three fluorophores with Cou480 acting as a relay fluorophore receiving energy from Py and transferring it to R6G. The different FRET scenarios between the three fluorophores in micelles provide a window for the generation of a matrix of colors, which occupies a significant 2D area in the chromaticity diagram, having potential applications in security



printing. The different fluorophoric ratios generate different colors based on their individual photonic emissions and the FRET processes taking place between them. Writing tests were carried out using varied ratios of the fluorophores in the micellar systems producing different colored outputs under the UV light with insignificant visibility under the white light. We envision that this as-discovered three fluorophoric FRET system could form the basis for the future development of multi-FRET lightharvesting devices and anti-counterfeiting security inks based on much simpler non-covalent interaction aided encapsulation of the fluorophores within the self-assembled soft systems.

1. INTRODUCTION

Fluorescence resonance energy transfer (FRET) is a distancedependent photophysical process by which energy is transferred nonradiatively from an excited fluorophore (donor) to a proximal ground state fluorophore (acceptor) by means of an intermolecular long-range dipole-dipole coupling. The applications of conventional single-step FRET systems are limited, as these provide localized color changes with outputs based on only one donor and one acceptor.¹⁻³ The multistep FRET systems, on the other hand, involve funneling of energy through a systematic array of three or more spatially oriented fluorophores⁴⁻⁷ having excellent usage in the development of photoluminescent materials with color tunability, photovoltaic devices, light emitting devices, multicolor bioimaging, photodynamic therapy, biosensing,⁸⁻¹⁰ and security printing.¹ In

order to achieve the spatial orientation of such multichromophoric arrays, scaffolds like DNA, dendrimers, proteins, and other biological assemblies have been used for inducing energy transfer utilizing either covalent or non-covalent interactions.⁸ Scaffolds promoting covalent linkages with chromophores are less relied upon due to them being laborious, time-consuming, and costly, their need for organic solvents for processing,¹² and above all the fact that they facilitate self-quenching and excimer formation which undesirably reduces the energy transfer efficiency. To overcome such limitations, there have been tremendous efforts to induce and

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Short communication

Cationic chiral surfactant based micelle-guided asymmetric Morita-Baylis-Hillman reaction

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1. Introduction

Morita-Baylis-Hillman (MBH) reaction is a powerful chemical transformation where simple starting materials are converted into highly functionalized molecular synthons in a catalytic process [1–2]. As a result this reaction has been applied to synthesis of natural products [3, 4], biologically relevant heterocycles [5,6] and more importantly in synthesizing versatile chiral building blocks [7–9]. However, the reaction has traditionally suffered from low reaction rates leading to limited substrate scope, but recent developments have focused on improving rates [10–14] and changed its scope considerably. In our own efforts towards synthesizing natural products using MBH-adducts as building blocks. we also suffered with its sluggish reaction rates and lower yields [15-18]. It is important to mention that over the years many chiral catalysts have been employed to develop asymmetric versions of MBH-reaction to produce variety of chiral building blocks. The diversity of chiral catalysts tested include Lewis acids and Lewis bases, Bronsted acids, thioureas, bulky ammonium salts, ionic liquids, phosphines and many more bi-functional organocatalysts including proline [19-22].

During the endeavour to increase efficiency of chemical reactions, micellar catalysis is gaining considerable attention among scientific community owing to their efficient outcome and involvement of green protocols [23]. These micellar environments are considered to be the nano-reactors having unique features that include isolation of the substrates from bulk solvent, enhancement of organic species

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solubilization in water, increase the local concentration and reactivity of reagents and promote chemo- regio- & stereo-selectivities [23,24]. Keeping in view these features of micellar-guided reactions, we earlier developed an expeditious protocol for MBH-reaction that utilizes the cationic surfactant cetyltrimethylammonium bromide (CTAB) as catalyst enhancing its reaction kinetics substantially. A plausible model was proposed that explains the stabilization of enolate-intermediate in the conjugate addition step of MBH- reaction through the positive charge on the self-organized aggregates of these cationic micellar structures thereby driving the reaction faster. To further capitalize on the utility of the micelles as catalysts in MBH-reaction, we sought to develop a generalized, fast and enantioselective variant of this reaction with the use of an enantiopure cationic surfactant, (1R,2S)-(-)-N-dodecyl-N-methylephedrinium bromide (DMEB) [25] which is expected to induce enantio-selectivity in addition to increase the reactions kinetics.

Cationic chiral surfactant (1R, 2S)-(-)-N-dodecyl-N-methylephedrinium bromide (DMEB) was utilized for the

first time in inducing asymmetry to Morita-Baylis-Hillman reaction in aqueous medium. Proton NMR studies car-

ried out to determine the locus of the reaction in micro-heterogeneous micellar environment, were found useful

in proposing a plausible model for asymmetric induction. This work demonstrates that under such mild and non-

hazardous reactions conditions, the reaction rates increase, good yields are favored and above all reasonable en-

2. Experimental

2.1. Representative procedure for MBH reaction of 4-nitrobenzaldehyde with acrylonitrile in presence of chiral DMEB surfactant

The micellar solution was prepared by dissolving DMEB (100 mg, 0.22 mmol) in distilled water (4 mL) and the resulting solution was stirred for 20 min at room temperature. To this solution, 4nitrobenzaldehyde (30 mg, 0.19 mmol), acrylonitrile (14 µL, 0.19 mmol) and DABCO (4 mg, 0.038 mmol) were added followed by continuous stirring till the reaction was over in 6 h. After the completion of reaction (monitored by TLC), the crude product was extracted with ethylacetate

ABSTRACT

antiomeric excesses are obtained.



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A novel combined chemical kinetic and trapping method for probing the relationships between chemical reactivity and interfacial H_2O , Br^- and H^+ ion molarities in CTAB/C₁₂E₆ mixed micelles⁺

Aijaz Ahmad Dar, 🕩 *^{ab} Laurence S. Romsted, 🕩 *^b Nighat Nazir, ^{bc} Yongliang Zhang, ^b Xiang Gao, ^b Qing Gu^b and Changyao Liu^d

A delicate balance-of-forces governs the interactions responsible for surfactant self-assembly and chemical reactivity within them. Chemical reactions in micellar media generally occur in the interfacial region of micelles that is a complex mixture of: water, headgroups, counterions, co-ions, acids or bases, organic solvents, and the reactants themselves. We have carried out a detailed study of a complex chemical reaction in mixed $CTAB/C_{12}E_6$ micelles by using the chemical kinetic (CK) and chemical trapping (CT) methods. The results provide a detailed quantitative treatment of the reaction of the anion of the antioxidant t-butylhydroquinone, TBHQ⁻, with 4-hexadecylbenzenediazonium, 16-ArN₂⁺, within the interfacial region of the mixed micelles in the $C_{12}E_6$ mole fraction range of 0 to 1 at three different total surfactant concentrations. CK experiments showed that this reaction is monophasic in $C_{12}E_6$ micelles, but biphasic in mixed micelles. The results were fully consistent with a complex mechanism in which TBHQ⁻ reacts with 16-ArN₂⁺ to give a transient diazoether intermediate that competitively breaks down into products and or reverts to starting materials. The kinetics are the same in mixed micelles of $CTAB/C_{12}E_6$ (grow) and $CTAB/C_{12}E_8$ (don't grow) showing that the rates only depend on micelle composition, not shape. CT results provided estimates of interfacial molarities of H₂O are approximately constant at ca. 39 and Br⁻ decreases from ca. 2.75 to 0.05 moles per liter of interfacial volume as $C_{12}E_6$ mole fraction increases from 0 to 1. Combined CK/CT results provided values for interfacial pH, ranging from ca. 4.25 in cationic micelles to 1.5 in nonionic micelles despite a constant bulk pH of 1.5 and the TBHQ interfacial $pK_a = 3.8$ at all $C_{12}E_6$ molar fractions. In totality, these results yielded an extraordinary amount of quantitative information about the relationships between the chemical reactivity and interfacial compositions of the mixed micelles.

1. Introduction

The noncovalent interactions responsible for the controlling the delicate balance-of-forces determining the physical properties of self-assembled surfactant mixtures, in particular ionic and nonionic surfactants, have been studied both theoretically and experimentally because of their distinctive physical properties

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The State University of New Jersey, New Brunswick, New Jersey 08854, USA. E-mail: romsted@rutchem.rutgers.edu compared to single surfactant systems.¹⁻⁴ Mixtures of nonionic surfactants with different chain lengths and head group sizes, e.g., oligooxy chains, tend to mix ideally, but mixtures of ionic and nonionic and anionic and cationic surfactants generally have properties that are far from ideality.1-4 These mixtures are important in terms of obtaining a fundamental understanding of the specific interactions governing their properties, but are useful for practical applications because they often show strong synergism on mixing that enhance solubilization efficiencies and surface tension reduction properties.⁵⁻¹¹ Other important properties investigated include the critical micelle concentration (cmc_{mix}), mixed micelle size and shape, solubilization characteristics and adsorption properties on liquid and solid surfaces.^{3,12-18} However, only a few investigations¹⁹⁻²⁵ describe the compositions of mixed micellar interfaces including interfacial water, counterion and nonionic headgroup molarities and additives such as alcohols, urea, and antioxidants.

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Research Article

Biological and computational studies of novel scaffolds of gallic acid: insight from density functional theory and molecular docking studies

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Abstract

In this study, we carried out the isolation of gallic acid from *Hippophae rhamnoides* plant followed by synthetic modification by using Dicyclohexyl carbodimide (DCC) as a coupling reagent. The synthetic modification involves the amidation of Gallic acid by a one-step protocol, converting gallic acid to its corresponding amide derivatives. The reactions involve a simple one-pot procedure with the formation of a chain of scaffolds of various beneficial amides in good to outstanding yields. The synthesized amides were characterized by several spectroscopic techniques like FTIR, HNMR, and Mass spectrometry. The synthetic derivatives were theoretically studied by Density Functional Theory (DFT) and their biological structural feasibility was studied by docking studies. Moreover, the antibacterial activities of the derivatives were also evaluated, and it is worthwhile to mention that all compounds have shown good antibacterial activity with the highest inhibition zone of 21 mm (A2) against strains of grampositive and gram-negative bacteria with MIC value of 40 μ g/mL.

Keywords

Gallic acid, Density Functional Theory, Molecular Docking, Antibacterial activity, *Hippophae rhamnoides*.

Introduction

Sea buckthorn (Hippophae rhamnoides L., *Elaeagnaceae*) is a thorny shrub that belongs to the family, *Elaeagnaceae*. It is a commercial crop of medicinal importance excessively found in the Ladakh region of Jammu and Kashmir, India¹. The plant is cataloged in the Chinese Pharmacopoeia, and its fruits and leaves are been used as traditional medicines in Tibet, Mongolia, and other nations in Central Asia^{2,3}. The parts of the plant are also a rich source of numerous bioactive compounds. Some of the bioactive compounds of Hippophae rhamnoids include phytosterols, polyphenolic compounds, coumarins and triterpenes ^{4,5}. Among different parts of plant, the leaves contain a large amount of coumarin, which can strengthen the function

of capillaries and has anti-coagulative, antispasms, and antipyretic effects ⁶. The peel of stem and fruit contains serotonin, whose occurrence in the plant kingdom is very rare and can act as a neurotransmitter. Moreover, this, the plant has received a number of epithets, including Wonder Plant, Ladakh Gold, and Golden Bush of Himalaya ^{7,8}. In context to the health benefits of plant, its pharmacological characteristics and phytochemical makeup have been thoroughly studied in relation to its potential medicinal uses from several decades ^{9,10}.

From past few decades, Researchers have isolated various bioactive compounds from the parts of plant. Phenolic acids were isolated from sea buckthorn's leaves. Gallic acid, p-coumaric acid, ferulic acid, 2-hydroxy-5-methoxybenzoic

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PDFelement

Isolation, characterisation, antifungal activity and validated UPLC/MS/MS method for quantification of novel compound from *Artemisia tournefortiana* Reichb

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ABSTRACT

Investigation into the chemical diversity of Artemisia tournefortiana resulted in isolation of one novel compound named tournefortin A and two known artemetin and tournefortin B bioactive compounds. Tournefortin B is first time obtained from natural source. The structure of all the isolated compounds were elucidated by detailed 1D and 2D NMR including HSQC, HMBC, ¹H-¹HOSY and NOESY spectroscopic techniques. Minimum inhibitory concentration (MIC) of all the tested compounds against tested fungal strains lies between 0.4 and 6.4 µg/mL and lowest MIC of 0.4 µg/mL of compound tournefortin A was found against Alternaria alternate. All the isolated compounds were quantified through UPLC/MS/MS and the developed method will serve as a first fingerprint method for the rapid determination of these phytomolecules in various plant extracts. Tournefortin B was found to be present in higher concentration. The higher antifungal effect of the isolated compounds suggests that this plant could act as potential source of antimicrobial agents.

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KEYWORDS

Artemisia tournefortiana Reichb; asteraceae; tournefortin A; UPLC/MS/ MS; antifungal activity

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Dielectric, magnetic and photocatalytic activity of PolyPyrrole/Prussian red nanocomposite for waste water treatment applications



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HIGHLIGHTS

- Poly pyrrole prussian red nanocomposite was synthesized by polymerisation method.
- Enhancement in thermal stability, a. c conductivity and magnitude of dielectric constant.
- Significant photocatalytically degradation of dyes was obtained.
- The adsorption studies reveal the selective adsorption capacity of the nanocomposite.
- Potential application for the recovery of precious metal ions from industry effluents.

ARTICLE INFO

Keywords: Adsorption Electromagnetic nanocomposite Dyes Antibiotic degradation a.c. conductivity Photocatalytic activity Dielectric constant Metal recovery

ABSTRACT

This work describes the synthesis and characterization of a novel nanocomposite of Prussian red and polypyrrole using standard protocols (Fourier-transform infrared spectroscopy, powder X-ray diffraction (XRD) and Transmission electron microscopy analysis). The comparative studies of the synthesized nanocomposite, pristine polypyrrole and related (PPY) nanocomposites with other dopants indicate an enhancement in the thermal, mechanical and electrical properties over pure ((PPY) and related PPY nanocomposites). The investigated physicochemical properties of nanocomposite suggest desirable material properties for environmental applications. The synthesized nanocomposite was observed to have a transition from paramagnetic to ferromagnetic behavior with a decreasing temperature and also displayed good photocatalytic activity towards dye and antibiotic degradation. The dye degradation of more than 80% under the pseudo-first order conditions as observed for, Methyl orange Methylene blue and Rhodamine B dyes in 80 min at room temperature and neutral pH. Besides, it showed photocatalytic activity towards the degradation of antibiotics: rifampicin, levofloxacin and amoxicillin with good results. Furthermore, the nanocomposite displayed selective adsorption capacity towards recovery of precious metal ions in the waste water.

1. Introduction

Currently conducting polymers have attracted much attention from scientific and engineering communities as versatile materials for a large number of applications ranging from polymer based electronics to biomedical tissue engineering. Conducting polymers like polypyrrole (PPY), polythiophene (PTP), polyaniline (PANI) are interesting materials for various important applications such as advanced electronic devices, electro chromic displays, drug delivery systems, chemical and biochemical sensors [1-9]. Among the family of conducting polymers, polypyrrole (PPY) is well known as the most promising member for a wide range of applications on account of its fine conductivity, electrochemical reversibility, chemical stability, good biocompatibility, ease of preparation and its possible tailoring to the specific needs of the material applications [10-12]. The properties of conducting polymers can be desirably tuned through the formation of their composites with

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PAPER



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Bioactive supra decorated thiazolidine-4carboxylic acid derivatives attenuate cellular oxidative stress by enhancing catalase activity†

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A pharmacophoric motif decorated with supramolecular functionalities (TZT) was designed for potential interaction with biological targets. Main insights of this work include the correlation of supra functionalities of TZT with its binding ability to proteins leading to the modulation of their structure and bioactivity as a promising perspective in the field of cellular protection from oxidative stress. To investigate the role of TZT in obliterating oxidative stress at a molecular level, its binding propensity with bovine serum albumin (BSA) and bovine liver catalase (BLC) was characterized using various biophysical methods. The binding constants of TZT with BSA ($K_b = 2.09 \times 10^5 \text{ M}^{-1}$) and BLC ($K_b = 2.349 \times 10^5 \text{ M}^{-1}$) indicate its considerable interaction with these proteins. TZT efficiently triggers favourable structural changes in BLC, thereby enhancing its enzyme activity in a dose dependent manner. The enzyme kinetics parameters of TZT binding to BLC were quantified using the Michaelis–Menten model. Both *in silico* and experimental results suggest that an increased substrate availability could be the reason for enhanced BLC activity. Furthermore, physiological relevance of this interaction was demonstrated by investigating the ability of TZT to attenuate oxidative stress. Treatment with TZT was found to mitigate the inhibition of A549 cell proliferation in the presence of high concentrations of vitamin C. This finding was confirmed at a molecular level by PARP cleavage status, demonstrating that TZT inhibits apoptotic cell death induced by oxidative stress.

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Introduction

Supramolecular chemistry, which involves molecular aggregation via non-covalent interactions, represents an attractive approach for understanding and targeting biological processes.¹ Indeed, the

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† Electronic supplementary information (ESI) available: Synthesis procedures, NMR, LCMS, Stern-Volmer plots and docking details. See DOI: 10.1039/ d0cp00253d

binding of bioactive molecules to their biological targets occurs primarily through supramolecular interactions,1-5 thus offering routes for the modulation of target-based drug development. In continuation of our interests in chemical biology,6-9 this work presents a comprehensive biophysical investigation of a synthesised pharmacophoric motif decorated with various supramolecular functionalities. Thiazolidine derivatives are remarkable compounds with a plethora of biological activities¹⁰⁻¹² that can be decorated with functionalities favouring supramolecular forces as potential ligands for biotargets.² With this motivation we synthesised (2S,4R)-3-(tert-butoxycarbonyl)-2-(2-hydroxyphenyl) thiazolidine-4-carboxylic acid referred to as the TZT molecule. The potential supramolecular interaction sites in the TZT molecule are depicted in Scheme 1. Main physical insights of this work are the ability of TZT to restructure proteins through complexation, thus enhancing enzyme activity and showing promising perspectives in the field of cellular protection from oxidative stress.

The increase in life expectancy is accompanied by a higher frequency of crippling degenerative diseases, thus triggering the need for new drugs. However, interactions with model proteins have to be considered while designing pharmacophoric molecules. Serum albumins are vital drug carriers determining

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Adsorptive avidity of Prussian blue polypyrrole nanocomposite for elimination of water contaminants: a case study of malachite green and isoniazid[†]

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Persistent water contaminants include a variety of substances that evade natural cleaning processes posing severe risks to ecosystems. Their adsorptive elimination is a key approach to safer attenuation. Herein we present the design and development of Prussian blue incorporated polypyrrole (PPY/PB) hybrid nanocomposite as a high-performance adsorbent for the elimination of malachite green (M.G.). isoniazid (INH) and 4-nitrophenol (4-NP) water contaminants. The nanocomposite synthesis was favored by strong dopant-polymer interactions, leading to a PPY/PB material with enhanced electro-active surface area compared to pristine PPY. The structure-activity response of the nanocomposite for the adsorption of target contaminants was unveiled by evaluating its maximum adsorption capacities under environmentally viable conditions. In-depth analysis and optimization of adsorption influencing factors (pH, temperature, and adsorbent dose) were performed. Using equilibrium studies, kinetic model fitting, aided with FTIR analysis, a multi-step mechanism for the adsorption of target contaminants on the nanocomposite was proposed. Furthermore, the PPY/PB nanocomposite also acts as a catalyst, enabling contaminant elimination following a synergistic scheme that was demonstrated using 4-NP contaminant. The synergetic adsorption and catalytic degradation of 4-NP using PPY/PB as adsorbent and catalyst was demonstrated in the presence of NaBH4 as a reducing agent in absence of light. In summary, this work highlights the targeted design of adsorbent, its optimization for adsorptive avidity, and the synergistic role of adsorption trapping in the catalytic degradation of persistent contaminants.

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Introduction

The quality of water resources is at risk with the release of persistent organic contaminants into the aquatic environment.1 These contaminants are characterized by high stability in water, which allows them to evade natural cleansing

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- † Electronic supplementary information (ESI) available: TGA, XRD, UV-Vis spectroscopy and adsortion studies. See DOI: https://doi.org/10.1039/d4cp01053a

processes, and water treatment protocols, leading to their ubiquitous environmental distribution, and even prevalence in municipal water distribution facilities.2 Owing to nonbiodegradability and chances of bio-accumulation, these contaminants pose serious health risks to humans and severe disturbances to aquatic ecosystems. For instance, the effluent discharges of the synthetic dye industry often contain a considerable amount of dyes even after general treatment. With an estimated annual dye production of 7.105 tonnes, the associated pollution concerns are significant.3,4 Among other chemicals, malachite green (M.G.) is widely used for dyeing cotton, wool, and silk fabrics.5 However, its runoff in effluent gives an aesthetically unpleasant colour to water and is bioaccumulative, a probable carcinogen, and toxic to aquatic organisms.6 Similarly, trace quantities of pharmaceuticals, particularly antibiotics from agricultural and livestock wastewater effluents, have been classified as emerging contaminants of major concern.⁷ The occurrence of antibiotics in the environment poses serious health risks such as the emergence of

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Full Length Article

Surface, optical and photocatalytic properties of Rb doped ZnO nanoparticles

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ABSTRACT

The present work describes the synthesis of pure and Rb doped ZnO (ZnO:Rb) nanoparticles by a simple combustion technique. The surface, structural, optical, morphology and photocatalytic activities of the ZnO:Rb nanoparticles were studied with respect to pure ZnO. X-ray diffraction studies confirmed the presence of a hexagonal wurtzite phase of ZnO and a secondary phase Rb₂ZnO₂ was also observed with increasing content of Rb into the ZnO. Field emission scanning electron microscopy confirmed an irregular shaped morphology for the ZnO:Rb samples. The X-ray photoelectron spectroscopy results confirmed both ZnO and Rb₂ZnO₂, as a new phase. Time of flight secondary ion mass spectroscopy revealed the homogeneous distribution of the Rb in the ZnO and the enrichment of Rb₂ZnO₂ at the outside and surface of the particles. In the photocatalytic degradation of RhB dye under natural sunlight irradiation, 97.0%, 20.2%, 16.6%, 15.7% and 12.8% degradation was evidenced for ZnO, Rb 5%:ZnO, Rb 7%:ZnO, Rb 10%:ZnO and Rb 15%:ZnO samples, respectively. The result demonstrated that doping ZnO with Rb affects the recombination process of the electron-hole pairs produced by the photon absorption and consequently influence the photocatalytic activity of ZnO.

1. Introduction

Researchers and scientists are currently paying a lot of attention to the environmental problems created by pesticides, different industrial effluents and likewise contaminants [1,2]. Environmental pollution has emerged as a global problem, therefore, it is imperative to work towards environmental protection with the development of modern science and technology. The dumping of wastewater is the major problem and has been disposed into rivers, lakes and water bodies without proper treatment, turning these natural water resources into obnoxious, odorous and aesthetically bad sewer channels with serious implications towards the development of our society [1,2]. It is worth noting that the untreated wastewater containing large amounts of organic as well as inorganic compounds, is a serious problem for the developing countries in the world. Therefore, it is a great challenge for the scientific community in the world to check/mitigate the water pollution level for the security of clean and safe water [1].

In the present era, semiconductor photocatalysts have fascinated the researchers over the past few decades due to their ability to solve the

growing environmental problems. ZnO nanostructures, with a direct bandgap of 3.37 eV belong to a versatile family of wurtzite n-type semiconducting materials having a large excitonic binding energy of 60 meV at 300 K. The appropriate band gap makes it a promising photocatalyst for the removal of the water pollutants, besides due to its non-toxic effect, wide direct bandgap, low cost, high photocatalytic activity and its stable structures [2–5]. Furthermore, ZnO has emerged as a promising semiconductor material due to its potential in the various fields like photocatalysis, chemical sensors, solar cells and bactericidal activities [3,4]. PDFelement

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The photocatalytic activity of the semiconducting material usually arises when they absorb light radiations (UV or visible, depending on the band gap) with energy greater than their band gap value and produces electron-holes pairs [5]. The electrons and holes can move towards the materials surface and interact with the adsorbed molecules to produce reactive species such as H_2O_2 , O_2^- and 'OH, respectively. These reactive species can easily oxidize and degrade organic contaminants into harmless compounds [5].

However, one of the major limitations of ZnO as a photocatalyst is

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Development of Polythiophene/Prussian Red Nanocomposite with Dielectric, Photocatalytic and Metal Scavenging Properties

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Hybrid materials of conducting polymers with coordination compound dopants offer a desirable combination of properties for targeted applications. This work presents polythiophene/prussian red (PTH/PR) nanocomposites as hybrid materials using PTH as a polymer matrix and PR nanoparticles as a readily available dopant with photo-reactive and magnetically active low-spin iron(III) complex. The PTH/PR nanocomposite was prepared by oxidative polymerization of thiophene monomers in the presence of PR nanoparticles. The synthesized material is characterized using Fourier transform infrared spectroscopy, powder x-ray diffraction and transmission electron microscopy. Comparative studies of the PTH/ PR nanocomposite indicate an enhancement in thermal and electrical properties compared with other PTH nanocomposites. The investigated physicochemical properties of PTH/PR suggest its suitability as a material for environmental applications, which were explored through dye photodegradation and metal ion recovery via adsorption studies. The PTH/PR nanocomposite degraded 65% of a methylene blue dye within 100 min by photo-oxidation, following pseudo-firstorder kinetics. It also displayed good adsorptive tendency towards precious metal ions including Au(III), Cu(II), Pd(II) and Ag(I). This finding suggests that PTH/PR nanocomposites could constitute potent nanomaterials for water treatment.

Key words: Conducting polymer nanocomposite, polythiophene, oxidative polymerization, physicochemical behavior, metal adsorption, dye degradation

INTRODUCTION

Conducting polymers are an interesting class of materials for various potential applications.1 The properties of conducting polymers can be desirably tuned via formation of hybrid materials with

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Shabnum Bashir and Syed Kazim Moosvi have contributed equally to this work

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appropriate inorganic dopants.^{2,3} Conducting poly-mer composites (CPCs) are hybrid materials composed of conducting polymers doped with coordination compounds offering desirable proper-ties for targeted applications.⁴ Compared with metals, CPCs are lighter in weight and more flexible, and can both reflect and absorb electromagnetic radiation.^{5–7} Such properties of CPCs make them suitable for applications including electromagnetic shielding, organic solar cells, batteries, supercapacitors, antistatic materials and other allied applica-tions.^{8,9} In that respect, the concentration of



* Unknown * | ACSJCA | JCA11.2.5208/W Library-x64 | manuscript.3f (R5.0.14:5005 | 2.1) 2021/01/05 13:43:00 | PROD-WS-120 | rg_3764838 | 1/30/2021 10:02:45 | 11 | JCA-DEFAULT



Organoselenium Compounds as Acetylcholinesterase Inhibitors: Evidence and Mechanism of Mixed Inhibition

3 Amit Kumawat, Shabnam Raheem, Fasil Ali, Tanveer Ali Dar, <mark>Suman Chakrabarty</mark>,* 4 and Masood Ahmad Rizvi*



5 ABSTRACT: Acetylcholinesterase (AChE) inhibitors are actively 6 used for the effective treatment of Alzheimer's disease. In recent 7 years, the neuroprotective effects of organoselenium compounds 8 such as ebselen and diselenides on the AChE activity have been 9 investigated as potential therapeutic agents. In this work, we have 10 carried out systematic kinetic and intrinsic fluorescence assays in 11 combination with docking and molecular dynamics (MD) 12 simulations to elucidate the molecular mechanism of the mixed 13 inhibition of AChE by ebselen and diphenyl diselenide (DPDSe) 14 molecules. Our MD simulations demonstrate significant hetero-15 geneity in the binding modes and allosteric hotspots for DPDSe on 16 AChE due to non-specific interactions. We have further identified 17 that both ebselen and DPDSe can strongly bind around the



is peripheral anionic site (PAS), leading to non-competitive inhibition similar to other PAS-binding inhibitors. We also illustrate the 19 entry of the DPDSe molecule into the gorge through a "side door", which offers an alternate entry point for AChE inhibitors as 20 compared to the usual substrate entry point of the gorge. Together with results from experiments, these simulations provide 21 mechanistic insights into the mixed type of inhibition for AChE using DPDSe as a promising inhibitor for AChE.

22 INTRODUCTION

²³ Acetylcholinesterase (EC 3.1.1.7) (AChE) is a serine protease, ²⁴ which plays a pivotal role in memory and cognition through its ²⁵ ability to hydrolyze the neurotransmitter acetylcholine to ²⁶ acetate and choline at cholinergic brain synapses.¹ Since its ²⁷ discovery, AChE has been extensively studied and has been the ²⁸ primary targets of insecticides and nerve agents.² Increasing ²⁹ evidence is found that correlate the activity of AChE to several ³⁰ neurodegenerative disorders including Alzheimer's disease ³¹ (AD), Parkinson's disease (PD), and so forth.^{3,4} Moreover, ³² the impairment of the cholinergic neuronal system in brain has ³³ been reported to be the underlying event of impairment of ³⁴ learning and memory in several animal models. Thus, ³⁵ inhibition of the AChE activity with the anticholinergic agents ³⁶ has therapeutic implications in countering diseases such as ³⁷ myasthenia gravis, glaucoma, and AD.^{5–7}

Several experimental and theoretical studies have been 38 Several experimental and theoretical studies have been 39 devoted to investigate the mechanism of inhibition of AChE by 40 the repertoire of AChE inhibitors (AChEIs).⁸⁻¹² Previous 41 structural studies have been shown to characterize the overall 42 structure of the enzyme into several subsites: the active site 43 (CAS) consisting of the catalytic triad, anionic subsite (AS), 44 and acyl binding pocket and the peripheral anionic site (PAS) 45 at the mouth of the gorge leading to the active site.^{13,14} 46 Interestingly, the active site is buried at the bottom of this narrow gorge lined with conserved aromatic residues. The 47 AChEIs have been found to either inhibit the enzyme through 48 covalent modification of the active site or by allosteric 49 regulation through significant conformational changes in the so enzyme. Several computational studies together with X-ray 51 crystallography have suggested the existence of multiple access 52 pathways to the active site that are implicated in substrate 53 entry or product release (Figure 1).15-17 In addition to the 54 ft main entrance/exit along the gorge, alternative routes such as a ss back door (involving residues W83, V129, Y446, and so forth 56 based on mAChE residue numbering; PDB ID: 1C2B¹⁸) and 57 side door (perpendicular to the gorge and comprising residues 58 from the omega loop) have been identified through molecular 59 dynamics (MD) simulations and multiple copy sampling 60 studies.^{19,20} Cheng and co-workers have identified dynamic 61 correlation between different subdomains in the protein and 62 the variation in the gorge radius.²¹ Recently, several allosteric 63

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Article

Visible-Light-Promoted Oxidative Annulation of Naphthols and Alkynes: Synthesis of Functionalized Naphthofurans

Neha Chalotra,^{||} Iftkhar Hussain Shah,^{||} Shabnam Raheem, Masood Ahmad Rizvi,* and Bhahwal Ali Shah*

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lation of naphthols with alkynes for the synthesis of functionalized naphthofurans has been developed. The reaction relies on the *in situ* formation of an electron donor acceptor pair between phenylacetylene and thiophenol as the light-absorbing system to obviate the requirement of an added photocatalyst. The protocol facilitates the transformation of 1-naphthol and 2-naphthol as well as 1,4naphthoquinone into a wide variety of highly functionalized naphthofurans.



INTRODUCTION

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Visible-light-driven reactions employing an in situ lightresponding system like an electron donor acceptor (EDA) can eliminate the traditional requirement of an external photocatalyst.1 The unique photo-physical properties of EDA complexes as ground-state supramolecular entities make these effective intrinsic photocatalysts toward emerging challenges of synthetic organic photochemistry.2 The EDA complex generated from the reaction ingredients, on light absorption, induces charge transfer from a donor to an acceptor molecule. If allowed by deactivation kinetics of the photoexcited complex, this initial charge transfer concludes in a single electron transfer (SET) process, generating reactive radical species as valuable synthons for novel synthetic routes.³ Thus, in continuation of our interests,⁴ herein, we developed a novel methodology highlighting EDA formation between phenylacetylene and thiophenol, thereby precluding the requirement of an external photocatalyst in the synthetic protocol (Scheme 1). This light-absorbing EDA complex was found to facilitate the site-selective coupling reaction of naphthols leading to the synthesis of highly functionalized naphthofurans. Notably, controlling site selectivity is particularly challenging in the case of 1-naphthol due to its equally nucleophilic ortho and para positions, with ortho being more sterically hindered.⁵ As an interesting observation of this methodology, we could switch selectivity between ortho and para positions by using a metal catalyst (FeCl₃), wherein without FeCl₃, 1-naphthol preferably reacted from the para position. Furthermore, the reaction was easily extendable to other related systems, viz., 2-naphthol and 1,4-naphthoquinone, giving highly functionalized naphthofuran derivatives along with the formation of a C-S bond. In its

essence, this method presents one step cascade of C–H activation and C–O bond formation followed by cyclization and C–S bond construction. Notably, benzo- and naphthofuran form a core skeleton of a large number of natural products, biologically active compounds, drug leads, and organic materials.⁶ Though many methods have appeared over the years addressing the synthesis of benzofurans,⁷ very few reports appeared for naphthofurans.^{8–10} Thus, the development of site-selective methods leading to the synthesis of naphthofurans remains an interesting challenge.

RESULTS AND DISCUSSION

We initiated our investigation by irradiating an equimolar mixture of 1-naphthol and phenylacetylene as model substrates in the presence of thiophenol, trifluoroacetic acid (TFA), and ferric chloride (FeCl₃) in CH₃CN under CFL. The reaction under stipulated conditions led to the formation of phenylnaphtho-[1,2-b]furan 1 in 69% yields (Table 1, entry 1). To establish feasibility in different solvents, the reaction was carried out in CH₃OH, toluene, DCE, DMF, and DMSO; while toluene and DCE gave the product in lower yields, no product formation was observed in other solvents (Table 1, entries 2–6). The light source change to blue light-emitting diodes (LEDs) gave the corresponding product in compara-

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Molecular interactions of diphenyldiselenide in DMSO and varied weight % of ethanol in DMSO solvent media at different compositions and temperatures (288.15 to 318.15)K

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ARTICLEINFO

ABSTRACT

Keywords: Diphenyldiselenide Density Viscosity Viscosity A and B coefficients

In the present work, volumetric, rheological, and thermodynamic analysis has been carried out for varied compositions of diphenyldiselenide in dimethyl sulfoxide/(5–25)% w/w of ethanol in dimethyl sulfoxide at seven distinct temperatures varying from 288.15 K to 318.15 K and ambient pressure (0.1 MPa). Through the acquired density data, the volumetric parameters such as apparent molar volume (V_{ϕ}), limiting apparent molar volume (V_{ϕ}), limiting apparent molar volume (V_{ϕ}), transfer molar volumes (V_{ϕ}^{o}), limiting apparent molar expansivity (E_{ϕ}^{o}), thermal expansion coefficient (u), and Hepler's constant (2c) were estimated. By the use of viscosity data, (viscosity A and B coefficients), viscosity B-coefficient of transfer (B_{σ}), change in viscosity B-coefficient with temperature and thermodynamic properties ($\Delta \mu_1^0, \Delta \mu_2^0, \Delta H_2^0$ and $T\Delta S_2^0$) were inferred. These parameters have aided in scrutinizing the various feasible interactions existing in the studied systems. From the explored results, we predicted that ion-hydrophillic / hydrophillic-hydrophillic interactions are predominant in the studied systems. Furthermore, through the positive sign of Hepler's constant and negative sign of change in viscosity B-coefficient with temperature values, we have inferred that diphenyldiselenide behaves as structure maker in dimethyl sulfoxide/(5–25)% w/w of ethanol in dimethyl sulfoxide.

1. Introduction

The element selenium is an essential micronutrient to animals and humans, acquired in organic/inorganic forms via foodstuffs primarily nuts, seafood, vegetables, meat, etc. [1]. It acts as a crucial component of immunological as well as antioxidant processes by promoting the functioning of selenoproteins. In humans, selenoproteins have a prominent role in the production of thyroid hormones, imprecise immune responses, oxidative stress responses, and vitality processes [2,3]. The cluster of selenoproteins is composed of three thioredoxin reductases and five glutathione peroxidases which are normally implicated in the oxidative stress response [4]. Generally, oxidative stress originates due to increased levels of reactive oxygen moieties, which are the predominant byproducts of numerous cellular processes. The equivalent composition and configuration of organoselenium compounds to selenoproteins allocate towards their probable action in subsiding the production of reactive oxygen species, in turn improving the antioxidant activity [5,6]. Diphenyldiselenide, a potential organoselenium

compound from symmetric aromatic diselenides possesses multitude of biological activities [7] and therefore participates in plethora of pharmacological activities such as antimicrobial, anticancer, antiinflammatory, neuroprotective, cytoprotective, and hepatoprotective effects in mammals [8-10]. The supramolecular propensity of diphenyldiselenidehas been explored for its chemico biological interaction with bioreceptors such as acetyl cholinesterase for a desired pharmacological response [11]. The type of functional groups, their steric attributes, solubility, and electronic effects collectively illustrate the widespread pharmacokinetic and pharmacodynamic efficacy of the drug compound. Analysing the molecular interactions of a bioactive compound with solvents bearing a range of polarity, dielectric constant, and hydrophobicity can be advantageous in predicting drug absorption, diffusion, and elimination. Consequently, solvent studies are strived to furnish vital descriptors for designing bioactive compounds as pharmacological target-binding drugs [12]. Keeping view of diverse pharmacological and synthetic applications of DPDSe, we envisaged its comprehensive physicochemical behavior density, and viscosity at over

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RESEARCH



Electronic structures and ligand effect on redox potential of iron and cobalt complexes: a computational insight

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Abstract

Density functional theory is applied to account the ligand effect on modification in the redox potential of coordination of three NN bidentate ligands (bpy/phen) to the metal ion $(Fe^{2+/3+}/Co^{2+/3+})$. Also, the role of the ligand framework for the stabilization of $[M(bpy/phen)_3]^{2+/3+}$ species is discussed in detail. In this work, we have found that the M^{2+} ions are more stabilized with the byp ligands while the M^{3+} ions are more stable with the phen ligands. The electronic structure and geometrical study disclosed the electronic configurations of the metal ions in both the possible spin states of a species. Furthermore, the HOMO–LUMO analysis demonstrates that the M^{3+} ion coordinated species have more energy gap as compared to the M^{2+} ion coordinated species. Among all the species, HOMO-LUMO energy gap has been found highest (4.62 eV) in the $[Fe(bpy)_3]^{3+}$ whereas lowest (3.28 eV) in the $[Co(phen)_3]^{2+}$ species. Additionally, we have also found that the bpy coordinated species have relatively higher redox potential value as compared to phen ligated species. Here we have noticed a close relationship between the redox potential and the optimized structural parameters of the studied species. Also, all the computed structural parameters of the studied species are in good agreement with the experimental data.

Keywords Iron/cobalt(II/III) complexes · Bpy/phen ligands · DFT · Electronic structures · Redox potential

Introduction

Bipyridine (bpy) and 1,10-phenanthroline (phen) are extensively used as chelating ligands in coordination chemistry [1]. Both these ligands were first described by Fritz Blau in 1888 [2–4]. The ligands bpy and phen construct five-membered chelating rings with the metal ion. Also, both these ligands have number of applications (such as photo-physical and photo-chemical) when they form chemical coordination with the transition metal ions [5–7]. These attractive applications/functionalities of bpy complexes are possible because of their structural diversity [8]. For example, Higuchi and coworkers recently reported coordination nanosheets (CONASHs) based on bpy ligand. These nanosheets are

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performing as a potential electrochromic material. These materials provide next-generation display applications [9]. Also, $[Ru(bpy)_3]^{2+}$ species is a well-known and well-studied compound that acts as a potent photosensitizer and has the capacity for solar energy conversion [10, 11]. This complex gave the neoteric path to researchers in the field of organic photon-initiative transformations. Currently, scientists have a center of interest to use this ligand for improvement in the efficiency of lithium-ion batteries [12] (see Scheme 1).

Similarly, 1,10-phenanthroline ligand also has many distinct properties based on its rigid structure in which the central ring fixes two N-atoms in juxtaposition [8]. Phen also has an entropic advantage, which means it can form rapid bonding with large-sized metal ions. This property has great importance towards the separation of lanthanide metal ions [13]. Another outgrowth of phen ligands interacts or binds with DNA and RNA, because of its planar structure. Phen also has a similar ability to bpy ligand to act as a triplet-state photosensitizer [8]. According to Shi and Nie's predictions based on theoretical investigations, phen can be helpful in the separation of heavy metals (lanthanides and actinides) [14]. Similar to bpy molecules, the different derivatives of phen can also be