



Ramakrishna Mission Residential College (Autonomous)

Kolkata 700103, WB, India

Collaborative research in synthetic and structural organic chemistry

Number 21

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Publication: Supramolecular self-assembly of structurally diversified ninhydrin-based molecules

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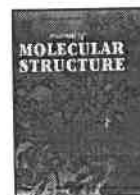
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Supramolecular self-assembly of structurally diversified ninhydrin-based molecules

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ABSTRACT

The present work discloses the self-assembly behaviour of differently substituted ninhydrin-based compounds in the solid state for the first time. Ninhydrin core with tunable functionalities generates varied noncovalent interactions leading to different supramolecular assembly. Single crystal X-ray diffraction study revealed that, ninhydrin-acetamide adduct 1 self-assembled to form corrugated sheet structure, whereas ninhydrin-*p*-cresol adduct 2 (*cis* dihydroxy hemiketal) containing water of crystallization was found to form water-mediated supramolecular helical architecture. On the other hand, easily achievable *N*-inserted ninhydrin derivative 3 derived from adduct 2 and *o*-aminophenol adopted helical arrangement in the crystalline state. Interestingly, novel cocrystal 4 obtained from adduct 2 was found to display helical motif through well directed hydrogen bonding with 2-aminopyridine. The supramolecular diversity arising due to the change in substitution of ninhydrin core structure was also reflected in scanning electron microscopy images.

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1. Introduction

Self-assembled supramolecular structures are ubiquitous in biological systems and biomaterials [1–6]. These types of structures are governed by non-covalent interactions like hydrogen bonding, hydrophobic and hydrophilic interaction, π -stacking, interaction between ionic groups [7–14]. In recent decades, wisely designed molecular building blocks have attracted intensive attention due to their unique supramolecular architecture, elegant morphology as well as their potential applications in diverse fields [1,15,16]. To date, extensive efforts have been invested for constructing such superstructures based on macromolecules, inorganic compounds and MOFs [17–23]. However, investigation of self-assembly process employing small organic molecules is relatively rare in supramolecular chemistry and crystal engineering [24–28]. For example, Khavasi et al. reported the formation of sheet structure involving halogen substituted naphthamide and quinoline carboxamide derivatives [24]. Helical structures employing small organic molecule (3,4,9,10-perylene-tetracarboxylic dianhydride) was demonstrated by Zhou and co-workers [27]. Recently, Sharma group successfully disclosed propensity of prolamide thymidine/uridine analogues towards typical helical motif [28]. Therefore, it remains a challenging and con-

tinuing task to accomplish small organic scaffolds exhibiting distinctive self-assembly behaviour.

On the other hand, self-assembly of cocrystals is of great interest due to their fascinating structural pattern as well as potential applications in medicinal chemistry, material science and host-guest chemistry [29–34]. Cocrystals are usually designed and synthesized in the form of crystalline solid comprising of two or more organic entities based on noncovalent interactions [35–41], among various type of cocrystal system, carboxylic acid-pyridine combinations are well established due to their potential application in drug discovery research [38–41]. However, reports on cocrystal exploiting aliphatic hydroxyl groups have rarely been witnessed [42]. In this context, ninhydrin-adducts containing hydroxyl groups with *cis* orientation may serve as promising candidate to assemble suitable pyridine system.

Ninhydrin (1,2,3-Indanetrione monohydrate) is a stable organic compound bearing *gem* dihydroxy groups at C-2 position which is flanked by two carbonyl groups. To date, much of the ninhydrin related research have been directed towards organic synthesis, traditional peptide chemistry and forensic sciences [43–47]. However, self-assembly study of ninhydrin derivatives remains under-investigated. A study by Medrud on the structure of ninhydrin revealed that the molecules of ninhydrin in the crystalline state are connected in layers by well directed hydrogen bonding [48]. This typical structural pattern could be diversified by introducing suit-

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able atoms/groups in ninhydrin core and thereby creating opportunity for interesting self-assembling propensity as well as surface morphology. As a part of our ongoing research [49–52], herein, we unveil the self-assembly behaviour and morphological studies of simple ninhydrin-derivatives by modulating the substitution pattern.

2. Experimental

2.1. Materials and physical measurements

All chemicals were purchased from commercial sources and used as received without further purification. Melting points were determined in open glass capillary and were uncorrected. TLC analyses were run on a Merck Kieselgel 60 PF₂₅₄ aluminium sheets. The spots were detected with UV light as well as with iodine. IR spectra were examined in KBr disc on a Perkin Elmer-L120–000A spectrometer. Proton magnetic resonance (¹H NMR) spectra were recorded on a Bruker Avance 300 and 500 spectrometer in DMSO-*d*₆ as solvent. X-ray diffraction was performed on Bruker AXS D8 QUEST ECO Diffractometer. Scanning electron microscopy (SEM) images were captured using a ZEISS EVO/LS10 instrument.

2.2. Synthesis of *N*-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)acetamide, **1**

A mixture of ninhydrin (1.0 mmol) and acetamide (2.0 mmol) was stirred in water (5.0 mL) at room temperature for 1 h. Then the solution was kept undisturbed for 7 days. The solid product separated was filtered and washed thoroughly with water. Recrystallization from methanol afforded compound **1** as colourless crystals. Yield: 85%, M.p. 190–192 °C, IR (KBr): 3366, 3046, 1763, 1725, 1634, 1523 cm^{−1}; ¹H NMR (300 MHz, DMSO-*d*₆) δ: 9.17 (1H, s, NH), 7.96–7.94 (5H, m, Ar-4H and OH), 1.78 (3H, s, Me). Anal. Calcd for C₁₁H₉NO₄: C 60.57, H 4.14, N 6.39; Found: C 60.67, H 4.25, N 6.27.

2.3. Synthesis of 4*b*,9*b*-dihydroxy-8-methyl-4*bH*-indeno[1,2-*b*]benzofuran-10(9*bH*)-one, **2**

A mixture of ninhydrin (1.0 mmol) and *p*-cresol (2.0 mmol) was refluxed in glacial acetic acid (5.0 mL) for 1.0 h. The reac-

tion mixture was then poured into ice cold water and kept undisturbed overnight. The solid product separated was filtered and washed thoroughly with water. Recrystallization from acetone afforded compound **2** as colourless crystals. Yield: 88%. M.p. 162–163 °C. IR (KBr): 3428, 1716, 1614, 1488, 1242 cm^{−1}. ¹H NMR (500 MHz, DMSO-*d*₆) δ: 9.55 (1H, s, Phenolic-OH), 8.17 (1H, s, OH), 8.08–8.03 (4H, s, Ar-H), 7.99 (1H, d, *J* = 8.0 Hz, Ar-H), 7.92 (1H, t, *J* = 8.0 Hz, Ar-H), 7.75 (1H, d, *J* = 8.0 Hz, Ar-H), 7.67 (1H, t, *J* = 7.0 Hz, Ar-H), 7.24 (1H, d, *J* = 1.0 Hz, Ar-H) 7.16 (1H, s, OH), 7.10 (1H, dd, *J* = 8.0, 1.5 Hz, Ar-H), 7.06 (1H, d, *J* = 7.5 Hz, Ar-H), 6.99 (1H, dd, *J* = 8.0, 2.0 Hz, Ar-H), 6.73–6.70 (2H, m, Ar-H and OH), 6.54 (1H, d, *J* = 8.0 Hz, Ar-H), 2.32 (3H, s, Me), 2.25 (3H, s, Me). Anal. Calcd for C₁₆H₁₂O₄: C 71.64, H 4.51; Found: C 71.48, H 4.63.

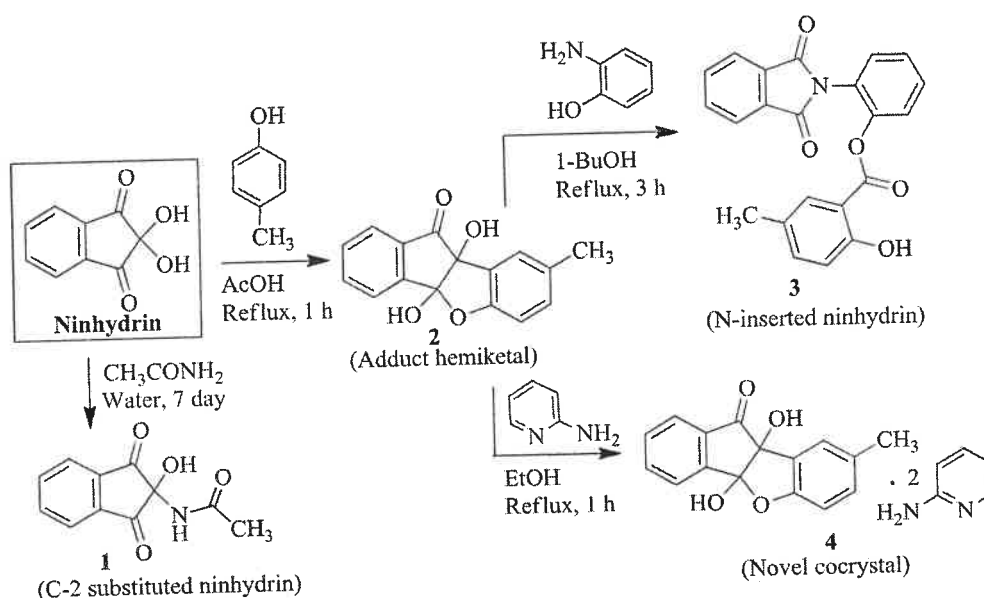
Ring open form of compound **2** remains in equilibrium with the cyclic hemi-ketal form in DMSO-*d*₆. The IR, NMR spectral data were compared with previous report [51].

2.4. Synthesis of 2-(1,3-dioxoisindolin-2-yl)phenyl-2-hydroxy-5-methylbenzoate, **3**

A mixture of adduct **2** (1.0 mmol) and *o*-aminophenol (2.0 mmol) was refluxed in 1-BuOH (5 ml) for 3 h. After completion of the reaction (TLC), the reaction mixture was cooled to room temperature and kept undisturbed overnight. The precipitated product was collected by filtration and washed with cold MeOH. Recrystallization from acetone afforded compound **3** as colourless crystals. Yield: 62%, M.p. 198–199 °C, IR (KBr): 3182, 1718, 1687, 1498, 1383 cm^{−1}; ¹H NMR (300 MHz, DMSO-*d*₆) δ: 10.32 (1H, s, Phenolic-OH), 7.95–7.88 (4H, m, Ar-H), 7.62–7.56 (4H, m, Ar-H), 7.50–7.45 (2H, m, Ar-H), 6.95 (1H, d, *J* = 7.0 Hz, Ar-H), 2.50 (3H, s, Me). Anal. Calcd for C₂₂H₁₅NO₅: C 70.77, H 4.05, N 3.75; Found: C 70.91, H 4.17, N 3.63.

2.5. Synthesis of cocrystal, **4**

A mixture of adduct **2** (1.0 mmol) and 2-aminopyridine (2.0 mmol) was refluxed in EtOH (5 ml) for 1 h. The reaction mixture was then cooled to room temperature and kept undisturbed. Slow evaporation of solvent within 2–3 days afforded colourless cocrystal **4**. Yield: 82%, M.p. 114–115 °C, IR (KBr): 3462, 3370, 3226,



Scheme 1. Synthesis of ninhydrin-based compounds 1–4.



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Collaborative

Collaborative research in synthetic and structural organic chemistry
Number 22

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Institute 2: Ramakrishna Mission Residential College (Autonomous)
Concerned Faculty: Dr. Prasanta Ghosh, Dept of Chemistry

Period of Investigation: 01-04-2018 to 30-04-2019

Project: Transition metal catalyzed organic transformation

Output: The result was published in a journal of international repute

**Publication: An Efficient Phosphotungstic Acid Catalysed Synthesis of 4, 5
Dioxopyrrolidines and Study of the Mechanistic Effect of the Solvent on the
Reaction**

Soumyadip Basu, Tanushree Ghosh, Suwendu Maity, Prasanta Ghosh and Chhanda
Mukhopadhyay

ChemistrySelect, 2019, 4, 5763-5767. DOI: 10.1002/slct.201901011

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Catalysis

An Efficient Phosphotungstic Acid Catalysed Synthesis of 4,5-Dioxopyrrolidines and Study of the Mechanistic Effect of the Solvent on the Reaction

Soumyadip Basu,^[a] Tanushree Ghosh,^[a] Suwendu Maity,^[b] Prasanta Ghosh,^[b] and Chhanda Mukhopadhyay^{*[a]}

An efficient protocol for the synthesis of dioxopyrrolidine scaffolds has been established using phosphotungstic acid as an effective catalyst in a multicomponent reaction of aromatic primary amines, dialkyl acetylene dicarboxylates and formaldehyde at room temperature in alcohol as a green

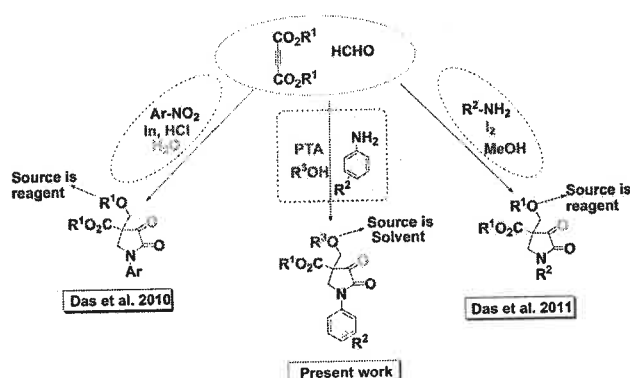
solvent. In this methodology, the reactant solvent has an important part and is involved in the reaction mechanism to increase the versatility of the product. This protocol involves environment friendly, cost effective methodology with a comparatively simple reaction mechanism.

Introduction

Pyrrolidines, being biologically important heterocycles, exhibit antifungal,^[1] antibacterial,^[2] and most importantly anticancer^[3] properties. Previous work that were reported^[4] for the synthesis of dioxopyrrolidines, generally involved higher reaction temperature, longer time period or hazardous catalysts. In one of those examples, Das and his group synthesised dioxopyrrolidines using HCl as catalyst.^[4c] In addition, in another report, they synthesised the same products using I₂.^[4d] Again, in few reports, the exchange of the functional groups of the alkynoates with the solvents was observed whereas, in some cases, the solvent did not attach to the product. In both the

reports of Das and his group, the solvent did not take part in the mechanism (Scheme 1). Although some previous work was done on the synthesis of this moiety, but the difference in the product formation concluded that detailed investigation of the mechanism of the reaction is yet to be disclosed. We studied the reaction in both possible ways, i.e. one in which chance of exchange of group and the other one where no exchange is observed. We have also tried various solvents and detected the effect of the solvent on the reaction. This study also increases the diversity of the synthesis of dioxopyrrolidines. In addition, we also explained the reaction mechanism in much simpler path than the previous reports.

Generally, heteropoly acids are oxygen acids where oxygen atom connects heteroatomic and multiatomic molecules through bridging ligand.^[5] These acids normally dissolve in small polar solvents like water, methanol, ethanol and acetone,^[6] but remain undissolved in non polar or macromolecular polar solvents. These acids have a very distinctive acidic property, and the acidity can be adapted according to the situation by altering the composition of the elements.^[7] It has strong acidic and redox properties. It also offers advantages of stable structure, high-speed regeneration, easy loading, noncorrosive nature, high activity, easy modification and low pollution^[8] and hence emerges as a type of enviro-friendly green catalyst.^[9] Heteropoly acid exhibits high catalytic activity in various reactions in both liquid-solid and gas-solid systems. One of the most widely studied heteropoly acid is phosphotungstic acid which has metal oxide as well as complex structures.^[10] Phosphotungstic acid (PTA) also, has a distinctive "pseudo-liquid phase" nature, which allows reactions to be taken place in both on the surface as well as inside the catalyst. Phosphotungstic acid is strongly acidic in solids and in solutions too, and retains a firmed Keggin structure^[11] in both the phases. Phosphotungstic acid has been used widely in both homogeneous and heterogeneous reactions^[12] because of its strong catalytic activity, superior selectivity, low reducibility, thermal stability and usability in mild conditions.^[13] For all these



Scheme 1. Synthesis of 4,5-Dioxopyrrolidines.

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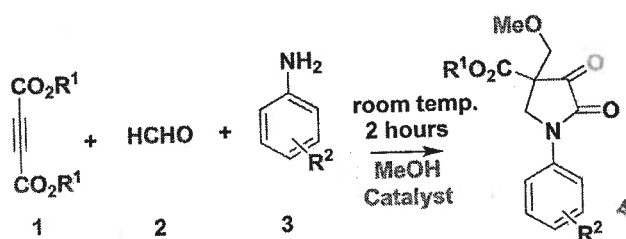
Supporting information for this article is available on the WWW under <https://doi.org/10.1002/slct.201901011>

combined reasons, we tried phosphotungstic acid as the acid catalyst in our present protocol and got sufficient good result.

Results and Discussion

We initially started the reaction in methanol solvent with aromatic amines, dimethyl acetylene dicarboxylate and excess of formaldehyde in presence of catalytic amount of phosphotungstic acid and got the desired products in high yield. However, we were not sure if exchange of the functional groups of the alkynoates with the methoxy group of the methanol was actually taking place or not.

To encounter this problem, we used diethyl acetylene dicarboxylate in place of dimethyl acetylene dicarboxylate, under exactly similar condition. We got the product containing one methoxy group which concluded that one ethoxy group of ethynoates is being exchanged with the solvent molecules. To confirm this conclusion, we have reacted various aromatic amines with diethyl acetylene dicarboxylate and excess of formaldehyde, and every time we have got the functional group exchanged product. This study (Scheme 2) established



Scheme 2. Synthesis of dioxopyrrolidines in methanol solvent.

that the solvent has sufficient effect in the mechanism of the reaction as well as in the product formation.

All the products synthesized in methanol given in Table 1.

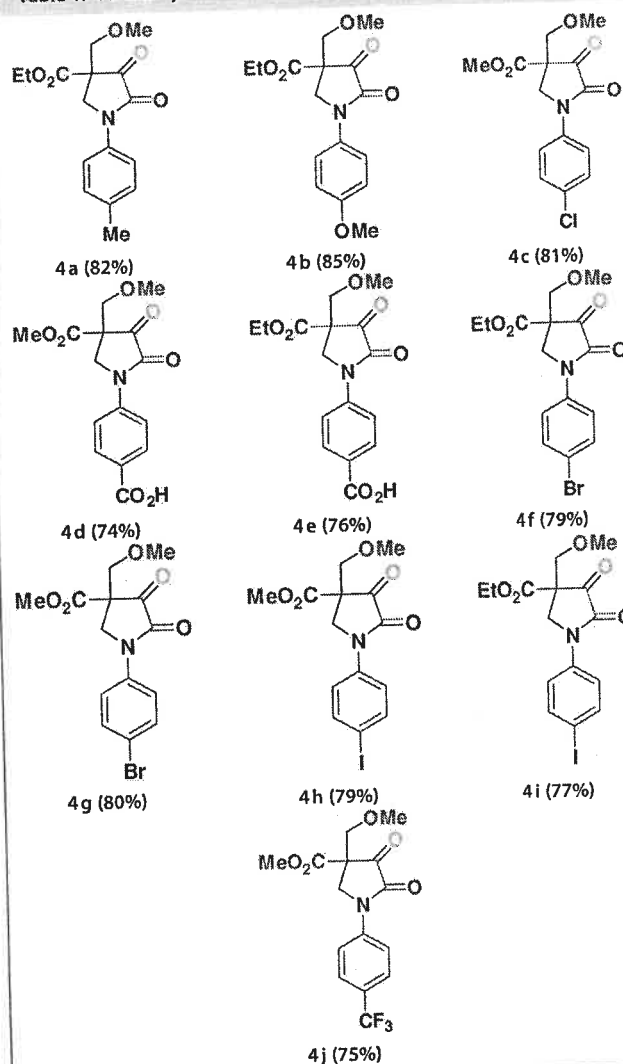
To further investigate this matter, we wanted to inspect the effect of higher order alcohols as solvent in this reaction (Scheme 3).

However, each and every time we got product where solvent molecule is part of the product. The products which are synthesized in higher order alcohol medium are given in Table 2.

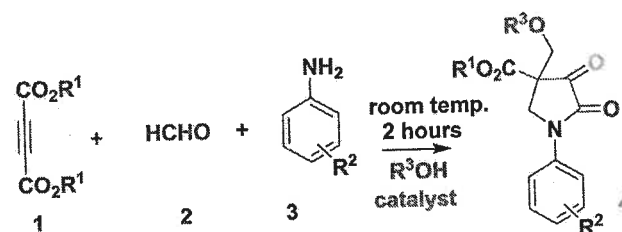
To From the all above observations, we suggest the following mechanism (Scheme 4).

From the mechanism we can say that in the reaction one functional group of the alkynoates is certainly not exchanged but undergoes elimination and one solvent molecule is attached with the product in the later stage. Proposed mechanism is also satisfied by the isolation of the intermediate C. The intermediate (4eC where, $R^1 = \text{Et}$, $R^2 = \text{COOH}$) corresponding to Product 4e is characterised by ^1H and ^{13}C NMR. Also an intermediate (4cC where, $R^1 = \text{Me}$, $R^2 = \text{Cl}$) corresponding to Product 4c is confirmed by single crystal X-ray diffraction. The intermediates were isolated after 30

Table 1. Various synthesized dioxopyrrolidines in methanol (4a–4j):^{a,b}



^aReaction condition: dialkylacetylene dicarboxylate [1, (1 mmol, 1 equiv.)], formaldehyde [2, excess] catalyst (.02 mmol, 1 equiv.) and Aromatic amine [3, (1 mmol, 1 equiv.)], were stirred in 7–8 ml methanol. ^bPure isolated yields.



Scheme 3. Synthesis of dioxopyrrolidines in higher order alcohol solvent.

minutes of the reaction and it was then treated with formaldehyde (1 mole) in alcohol solvent which resulted in the formation of corresponding products.

To further establish the reaction mechanism we carried out this reaction in other solvents like water, toluene, acetonitrile



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Institute 2: Ramakrishna Mission Residential College (Autonomous)
Concerned Faculty: Dr. Prasanta Ghosh, Dept of Chemistry

Period of Investigation: 04-07-2018 to 30-03-2019

Project: Zeolite catalyzed organic transformation

Output: The result was published in a journal of international repute

Publication: Na-Y Zeolite, a convenient and recyclable catalyst for the facile one-pot synthesis of spiro dibenzo[*b,e*][1,4]oxazepine scaffolds

Kajal De, Suvendu Maity, Prasanta Ghosh and Chhanda Mukhopadhyay

Applied Organometallic Chemistry, 2019, 33, 1-12. DOI: 10.1002/aoc.4852


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FULL PAPER

Na-Y Zeolite, a convenient and recyclable catalyst for the facile one-pot synthesis of spiro dibenzo[*b,e*][1,4]oxazepine scaffolds

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A new method for the synthesis of Spiro dibenzo[*b,e*][1,4]oxazepines that involves a three-component reaction of isatins, 2-amino phenols and cyclic-1,3-diketones has been developed. This protocol employs Na-Y zeolite nanopowder as a heterogeneous catalyst and does not require the presence of any additives or strong acid-base condition. Na-Y zeolite nanopowder was synthesized through a simple hydrothermal procedure and it was characterized using different array of sophisticated techniques. Key features of the reaction include a recyclable catalyst and a wide scope of possible substrates.

KEYWORDS

isatin, nanopowder, oxazepine, recyclable, zeolite

1 | INTRODUCTION

Among various N and O containing heterocyclic compounds oxazepines have received much attention owing to their broad spectrum of biological and pharmacological activities. In oxazepines, benzoxazepine derivatives shows vast variety of biological activities like antibacterial,^[1] antifungal,^[2] hypnotic muscle relaxant,^[3,4] antagonistic,^[5] antiinflammatory, telomerase inhibitors^[6] and antiepileptic.^[7] Moreover, dibenzo[1,4]oxazepines also act as a potent progesterone receptor antagonists, p38 MAP kinase inhibitors, TRPA1 ion channel modulators and histone deacetylase inhibitors.^[8] Tricyclic systems containing the 1,4-oxazepine ring have antipyretic and antiphlogistic activities,^[9] whereas pyrazole containing 1,4-oxazepine nucleus showed anti-inflammatory^[10] properties. Pyrido-1,4-benzoxazepines are used in the treatment of depression in mammals and also be useful for memory dysfunction which associated with reduced cholinergic function in Alzheimer's disease.^[11] Besides, 1,4-benzoxazepine derivatives also act as an antipsychotic^[12] agents and Pyrido fused [1,4]

benzoxazepines are useful in the treatment of HIV-1.^[13] Figure 1

There are several traditional strategies for the synthesis of benzoxazepines via condensation reactions of 2-aminophenols with α , β -unsaturated carbonyl compounds, β -ketoesters, benzoyl chlorides, benzoic acid and isocyanides.^[14–17] These reaction methods can produce benzoxazepines effectively. However, they inevitably suffer from several drawbacks like multistep reaction procedure, poor yield and therefore low atom economy. Thus, from the sustainable and atom-economic point of view, it is still highly desirable to develop alternative approaches for the synthesis of 1,4-benzoxazepines with higher atom economy.

Spirooxindole subunits are widely found in many synthetic pharmaceuticals and natural products and this spiro heterocyclic ring systems when attached to a single molecule increases biological activity to a greater extent. Isatin and its derivatives have been widely used as a versatile starting material for the synthesis of this spirooxindole containing spiro compounds.^[18–21] So, it is a challenging at the same time interesting to construct

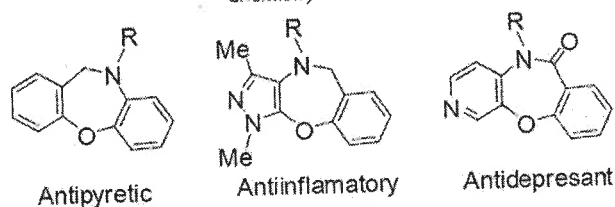


FIGURE 1 Examples of biologically active oxazepines

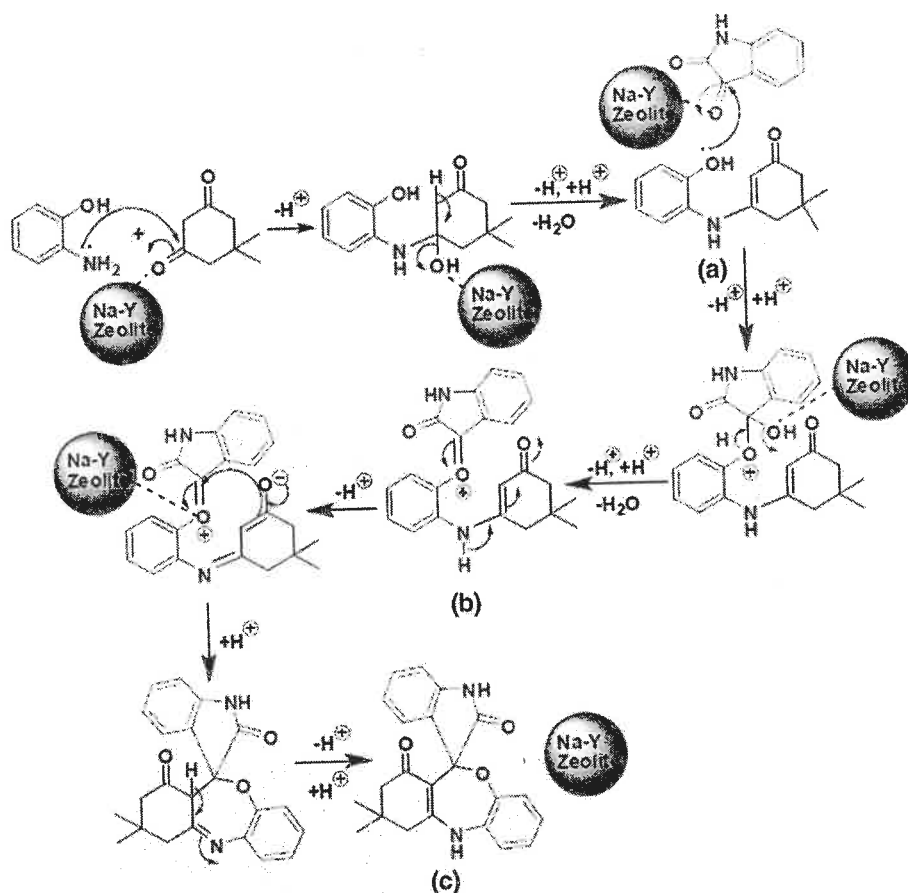
spiro-fused dibenzo[*b,e*][1,4]oxazepine derivatives by employing new methods. The development of new strategies based on recyclable heterogeneous catalysts which minimizes the dispersions of harmful chemicals in the environment and maximizes the use of renewable resources can result in significant economic and environmental benefits.^[22–25] In this context, we have developed a new type of heterogeneous Na-Y Zeolite catalyst which is very effective both in terms of the reaction time as well as the percentage of yield. Besides, the catalyst can be easily recovered and the reusability of the catalyst is quite high. Zeolites are highly versatile molecular sieve from the faujasite family of zeolites whose three-dimensional

pore structure and solid acidity make it useful as a catalyst.^[26–31]

2 | EXPERIMENTAL

2.1 | Materials and instrumentation

All the starting material were purchased from available commercial sources and used without purification. The reactions were performed in an water bath under reflux condition in a round-bottomed flask and improvement of the reaction was checked by TLC using silica gel. ¹H and ¹³C spectra were measured on Bruker 300 MHz instrument using DMSO-*d*₆. Melting points were recorded under electrical melting point apparatus with an open capillary. IR spectra were obtained from the Perkin Elmer Spectrophotometer RX/FT- IR system. The C-H-N-analyses were carried out on a 2400 Series II CHNS Analyzer, Perkin Elmer USA. X-ray diffraction was performing on a Bruker SMART diffractometer. X-ray diffraction patterns of the powder sample were



SCHEME 1 A probable mechanistic pathway for the synthesis of Spiro dibenzo[*b,e*][1,4]oxazepine derivatives catalyzed by Na-Y zeolite nanopowder catalyst



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Concerned Faculty: Dr. Prasanta Ghosh, Dept of Chemistry

Period of Investigation: 01-02-2018 to 28-02-2019

Project: TiO_2 Nanoparticles and the Catalytic activities in Synthesis of N-Substituted Pyrroles

Output: The result was published in a journal of international repute

Publication: Creation of DABCO Based Amphoteric Ionic Liquid Supported TiO_2 Nanoparticles: Execution of Amplified Catalytic Properties on Microwave Assisted Synthesis of N-Substituted Pyrroles

Priya Mondal, Sauvik Chatterjee, Asim Bhaumik, Suvendu Maity, Prasanta Ghosh and Chhanda Mukhopadhyay

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Catalysis

Creation of DABCO-Based Amphoteric Ionic Liquid Supported TiO₂ Nanoparticles: Execution of Amplified Catalytic Properties on Microwave-Assisted Synthesis of N-Substituted PyrrolesPriya Mondal,^[a] Sauvik Chatterjee,^[b] Asim Bhaumik,^[b] Suwendu Maity,^[c] Prasanta Ghosh,^[c] and Chhanda Mukhopadhyay^{*[a]}

This is the first report of DABCO based amphoteric ionic liquid supported TiO₂ nanoparticles, a supported catalyst with an ionic liquid layer (SCILL). It is highly efficient, recyclable, quasi heterogeneous catalyst for microwave assisted solvent free synthesis. Highly polar DABCO based ionic liquid with high dielectric constant of titanium dioxide nanoparticles enables the system as efficient microwave irradiation absorber. Amplified catalytic properties of this new combined green catalytic system have been first time implemented for the chromatography-free synthesis of highly functionalised pyrrole moieties under microwave assisted solvent-free conditions. The generation of catalyst and ionic liquid capping over titanium dioxide

nanoparticles were characterised via Scanning Electron Microscopy (SEM), High Resolution Transmission Electron Microscopy (HRTEM), Thermo Gravimetric Analysis (TGA), Dynamic Light Scattering (DLS), Powder X-Ray Diffraction (PXRD), Energy Dispersive Analysis X-ray (EDAX) and Fourier Transform Infrared Spectroscopy (FT-IR spectra). This combined quasi heterogeneous twin catalytic system, containing both acidic and basic environment afford the desired products in excellent yields within short reaction time. Here, the catalytic effect featuring the synergetic effect of titanium dioxide nanoparticles and amphoteric DABCO based ionic liquid were magnificently tethered.

Introduction

Upcoming world will have to face the question of existence until or unless we follow environmentally benign conditions throughout our practice. Hence, green synthetic procedure deserves high importance in synthetic organic chemistry. For a better future, synthetic organic chemists should focus on lesser energy consumption and less hazardous condition.^[1] Therefore, our focus leaned on establishment of green and sustainable synthetic procedure. Now, it is not possible to perform all the reactions at room temperature hence the reaction mixture needs to be heated in high temperature. In order to lower the energy consumption, microwave irradiation is very high-quality alternative of conventional heating as it provides rapid, homogeneous and competent dielectric heating that results in much quicker reaction rate and also lower energy consumption

than conventional heating.^[2] The traditional heating required 3–9 times additional energy than the microwave assisted organic synthesis (MAOS).^[3] Additionally microwave-assisted reactions performed at an optimized reaction temperature found to be cleaner and also lead to less by-products.^[4]

To attain sustainability, whole world is trying to avail environmentally benign conditions as much as possible.^[5] Organic chemists are not exclusion. Hence, apart from using microwave irradiation, we also emphasised to set up a solvent-free methodology. A solvent free reaction system has several advantages such as cost-effectiveness, environmentally benevolent condition, large reduction in reactor size and higher reaction rate due to greater contact of reactant with energy source.^[6]

Next to achieve a successful solvent-free microwave assisted multicomponent reaction pathway, we focused on the synthesis of an unique catalytic system that will not only play an efficient role of catalyst, but also act as a very good reaction medium. As microwave irradiation is absorbed efficiently by polar compounds, ionic liquid could be the best choice for this purpose. Ionic liquids are highly polar in nature having higher boiling point and lower vapour pressure.^[7] There are already previous reports where synergistic effect of MW and IL were utilized.^[8] Since ionic liquids are expensive, a large extent of catalysis research is based on ideas where ionic liquids can be exercised scarcely by applying a little amount, immobilized as a skinny coat onto a support system.^[9] Supported catalysts with an ionic liquid layer (SCILL) is one of the admired concepts.^[10]

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Based on this concept, in our previous work, we have utilized the symbiotic catalytic effect of imidazolium based ionic liquid and zinc oxide nanoparticles (NPs) successfully.^[11] Inspired by that work, our effort was to design a more efficient ionic liquid immobilised metal oxide nanoparticles system that would catalyze microwave assisted solvent-free reactions as well. Consequently TiO_2 nanoparticles were chosen as support system and DABCO based amphoteric ionic liquid was chosen as coating agent. DABCO based ionic liquids itself showed good catalytic properties in many recent organic synthesis.^[12] Here we have reported an interesting DABCO based mono substituted ionic liquid where both acidic and basic catalytic site was present. It is pleasing to inform that we have reported this DABCO based ionic liquid $([\text{DABCO}-\text{C}_2\text{COOH}]^+[\text{Br}]^-)$ for the first time. Unique feature of this DABCO based ionic liquid is that it contains both acidic (hydrogen containing quaternary Nitrogen) and basic catalytic site (carboxylate anion) within one system, such type of amphoteric ionic liquid is rarely available. Using this newly reported $[\text{DABCO}-\text{C}_2\text{COOH}]^+[\text{Br}]^-$, we were able to prepare $[\text{DABCO}-\text{C}_2\text{COOH}]^+[\text{Br}]^-$ immobilized TiO_2 NP, here titanium tetraisopropoxide acted as precursor. During the synthesis of this SCILL, in situ generation of TiO_2 nanoparticles occurred.

As the core of the catalytic system consisted by TiO_2 NPs, it helps the system to be quasi heterogeneous and also poses acidic environment.^[13] TiO_2 NP has a high dielectric constant of nearly 50, which implies absorption power of MW irradiation is very well, getting superheated above the solvent bulk temperature.^[14] Here in situ generation of TiO_2 nanoparticles occurred from titanium tetra isopropoxide where $[\text{DABCO}-\text{C}_2\text{COOH}]^+[\text{Br}]^-$ acted as stabilizer. Ionic liquid coating over TiO_2 NPs makes it also highly competent for microwave irradiation absorber as ILs having polar compounds acted as very efficient microwave irradiation absorber.^[15] Additionally, carboxylic group functionalised mono-substituted DABCO based ionic liquid possesses both acidic and basic environments to promote various efficient organic synthesis. All these advantages of this combined catalytic system make the catalyst novel and exceptionally applicable towards organic protocols.

Our next challenge was the application of synthesized catalyst for the synthesis of a series of heterocyclic moiety and also exploration of catalytic activity of the catalyst. Now among heterocyclic moieties, pyrroles have a prominent position in the chemistry as it is the key structural fragment of living organisms like porphyrins, the chlorins, and the corrins found in, respectively, heme, chlorophyll and vitamin B12.^[16] Moreover, they are considered as crucial structures by synthetic chemists because of widespread applications in pharmaceuticals and materials science.^[17] Pyrrole is the core structural motif or important skeleton of valuable drugs like top-selling cholesterol-lowering agent atorvastatin, the anticancer drug sunitinib or talimustine, the anthelmintic agent pyvinium, the analgesic drug zomepirac and the anti-inflammatory drug tolmetin.^[18] Additionally, pyrrole-derived compounds acted as very good anti-HIV, antibacterial, antifungal, antitumoral, anti-malarial and antioxidant agent.^[19] In addition, pyrroles have lots of application like polypyrroles can be utilized as conducting

materials in the preparation of electroluminescence devices, and pyrrolic macrocycles employed as anion receptors.^[20] Pyrrole containing molecules are also effective as COX-1/COX-2 inhibitors and cytotoxic activity against a variety of marine and human tumor models.^[21]

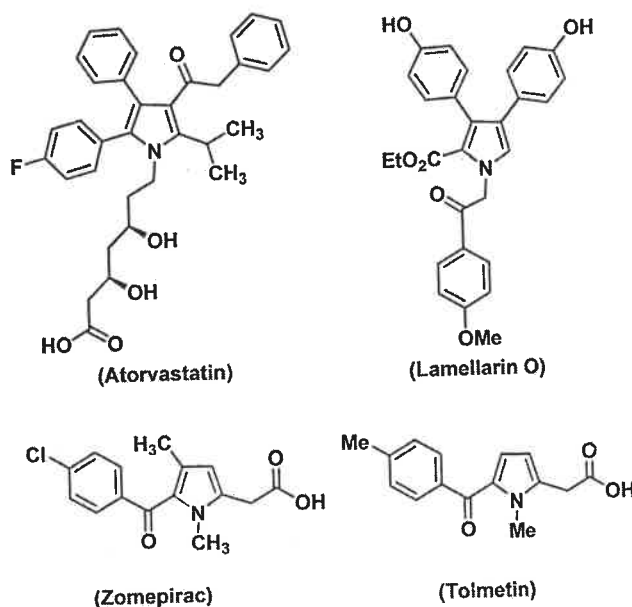


Figure 1. Few representative structures of Pyrrole based drugs

As a result, several synthetic methodologies have been developed for the synthesis of pyrrole moieties, including traditional methods such as Hantzsch, Knorr, Piloty–Robinson, Paal–Knorr, Van Leusen and Barton–Zard.^[22] Depending on pervasive applicability, development of pyrroles have moved a lot in the past decades, and include metal-catalyzed cyclization, rearrangement of o-vinyl oximes, multicomponent coupling reactions, cycloaddition methods, oxidative coupling reactions, olefin cross-metathesis, isocyanide-based reactions, rearrangement reactions, hydroamination of diynes, and aza-Wittig reactions and several others.^[23] Although numerous methods for the synthesis of pyrroles are effective, the development of environmentally benign reaction condition that lead directly to multisubstituted pyrroles from basic chemicals within a very short time with substantial yields still remains a confront to synthetic chemists. In particular, N-aryl pyrrole derivatives exhibit a variety of interesting biological and biomedical properties.^[24] Therefore, the development of efficient and novel synthetic method to construct highly-functionalized N-substituted pyrrole derivative is strongly desired.

Hence our newly synthesised TiO_2 supported DABCO based ionic liquid $(\text{TiO}_2-[\text{DABCO}-\text{C}_2\text{COOH}]^+[\text{Br}]^-)$ were applied to produce N-substituted Pyrrole moieties via two different schemes. It was pleasing to note that by using $\text{TiO}_2-[\text{DABCO}-\text{C}_2\text{COOH}]^+[\text{Br}]^-$, we were able to derive a solvent free, chromatography free, microwave assisted protocol for N-substituted Pyrroles within few minutes. Although there were



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Collaborative research in synthetic and structural organic chemistry
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Period of Investigation: 01-01-2018 to 30-11-2018


Project: Acid-promoted multicomponent allylic amidation towards 7-acetamido tetrahydroindole derivatives

Output: The result was published in a journal of international repute

Publication: Acid-promoted multicomponent allylic amidation towards 7-acetamido tetrahydroindole derivatives

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Tetrahedron letters, 2019, 60, 435-438. DOI: 10.1016/j.tetlet.2018.12.068

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Accepted Manuscript

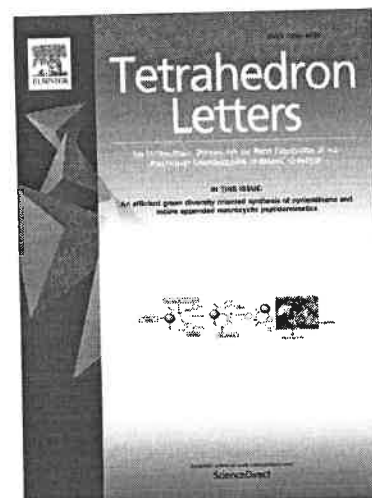
Acid-Promoted Multicomponent Allylic Amidation towards 7-acetamido tetrahydroindole derivatives

Sayan Pramanik, Suvendu Maity, Prasanta Ghosh, Chhanda Mukhopadhyay

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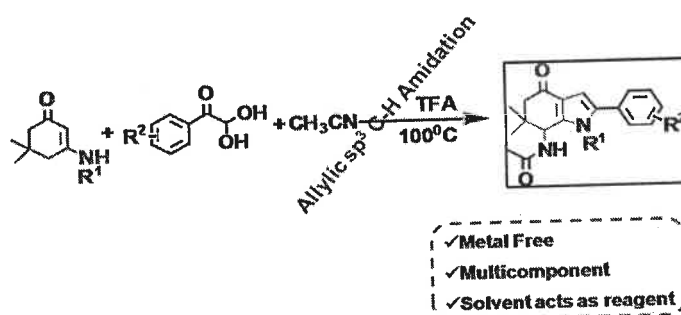
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Graphical Abstract

Acid Component Multicomponent
Allylic Amidation towards 7-acetamido
tetrahydroindole derivatives.

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Sayan Pramanik, Suwendu Maity, Prasanta Ghosh and Chhanda Mukhopadhyay*





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Collaborative research in synthetic and structural organic chemistry
Number 26

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Period of Investigation: 04-01-2017 to 30-11-2018

Project: Organocatalysis and functionalization

Output: The result was published in a journal of international repute

Publication: Pseudo five component reaction towards densely functionalized spiro[indole-3,2-pyrrole] by picric acid, an efficient syn-diastereoselective catalyst: insight into the diastereoselection on C(sp³)-C(sp³) axial conformation

Ayon Sengupta, Suwendu Maity, Animesh Mondal, Prasanta Ghosh, Sonali Rudra
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Organic & Biomolecular Chemistry, 2019, 17, 1254-1265. DOI:
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Pseudo five component reaction towards densely functionalized spiro[indole-3,2'-pyrrole] by picric acid, an efficient *syn*-diastereoselective catalyst: insight into the diastereoselection on C(sp³)–C(sp³) axial conformation†

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A new series of highly-functionalized spiro compounds of pyrrole were synthesized by a one pot, step-economic condensation of isatin, arylamine and β -keto ester catalyzed by wet picric acid. Initially, the reaction was proposed with an expectation of the formation of a multi-spiro heterocyclic framework of highly-substituted piperidine. However, the isomeric compound was characterized to be a five-membered pyrrole derivative with a diverse scope of variations having different types of substituents in the three components respectively. The possibility of formation of various diastereomers around the hindered single bond and the spiro carbon was limited, as only *syn* products **syn-60** and **syn-60'** were isolated in all the reactions performed under the standard conditions. Probably the reactions were mediated by the *si-facial* formation of the bonds in a picric acid stabilized charge transfer complex transition state. Also, the manner a molecule achieves the most stabilized energy minimized arrangement with all its substituents in space was studied by DFT calculations where **syn-60** was more stable than **syn-60'**. The studies on the formation of **syn-60** and **syn-60'** were carried out by variation of electronic and steric factors in each of the components of the reactions.

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Introduction

Isatin and its metabolites are constituents of many pharmacological agents and natural alkaloids,¹ drugs,² dyes,³ pesticides and analytical reagents. They are also components of many synthetic compounds exhibiting a wide range of effects, including antiviral,⁴ antitumor, anti-angiogenic,⁵ anti-bacterial,⁶ anti-HIV,⁷ anti-fungal,⁸ anti-convulsant⁹ and anti-inflammatory¹⁰ activities. Isatin itself is an endogenous oxidized indole with a wide spectrum of behavioural and metabolic effects. It has a distinct and discontinuous distribution in the brain, peripheral tissues and body fluids and isatin

binding sites are widely distributed with increased output during stress. Its most potent known *in vitro* actions are as an antagonist of atrial natriuretic peptide (ANP) function and NO signalling.¹¹ The construction of multi-spiro heterocyclic frameworks *via* its highly-reactive prochiral C-3 carbonyl group has been a challenging endeavour for synthetic chemists as it requires a synthetic design based on 1,3-dipolar cycloaddition reactions,¹² Morita–Baylis–Hillman reaction,¹³ Mannich/Pictet–Spengler sequence¹⁴ and other cyclization reactions such as photo-induced reactions¹⁵ and electrocyclization.¹⁶ There are several reports on the synthesis of mono-spiro-heterocycles leading to five-, six- and seven-membered heterocyclic frameworks.¹⁷

Nevertheless, fusion of two or more isatin moieties in a single framework leading to molecular complexities of multi-spiroheterocycles¹⁸ has always been interesting and opens up a versatile area of research. The use of an MCR strategy has become the most widely used method for the synthesis of various spiro-oxindoles.¹⁹

These reactions provide instantaneous access to large compound libraries with diverse functionalities and offer significant advantage over time consuming conventional linear type

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† Electronic supplementary information (ESI) available: Detailed experimental procedures and full spectroscopic data of all the newly synthesized compounds. CCDC 1846235, 1846236 and 1846234. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8ob02849d

synthesis. After reviewing several reports on the synthesis of highly-substituted piperidines by MCR methods using a variety of organocatalysts²⁰ and other acid catalysts²¹ that are available in the literature, we attempted to synthesize initially the spiro-oxindole involving a piperidine moiety (Probability 1, Scheme 1) by reaction of arylamines, isatins and β -keto esters. During the course of our study, however the X-ray crystallographic data supported by structural elucidation experiments of NMR concluded the formation of an isomeric five-membered pyrrole instead of a six-membered piperidine ring. We established the structure of spiro[indole-3,2'-pyrrole] where one isatin molecule was fused to the C-3 of the pyrrole ring and another isatin molecule was attached to the C-4 of the pyrrole ring with a single bond leading to a monospiro-tetrahydrospiro[indole-3,2'-pyrrole] system (Probability 2 and 2', Scheme 1). Similar spiro[indole-3,2'-pyrrole] derivatives are usually useful as antitumor agents and are reported to have moderate to potent high antitumor activity against the HEPG2 (liver cancer) cell line (IC_{50} = 12.16 mM) compared to that of doxorubicin (IC_{50} = 7.36 mM) and some compounds revealed moderate antitumor properties against human cell lines, HCT116 (colon), MCF7 (breast), HEPG2 (liver), A549 (lung), and HeLa (cervical).²² Some derivatives showed significant inhibition of p53-Mdm2 protein-protein interaction and the PDE4B enzyme *in vitro*.²³ Such type of core structure was reported by one-pot MCR with arylamines, isatins and acetone in acetic acid,²⁴ using a nano $MgBi_2O_4$ catalyst in water²⁵ and isoxazole, isatin and acetone in THF using a catalytic amount of CAN.²⁶

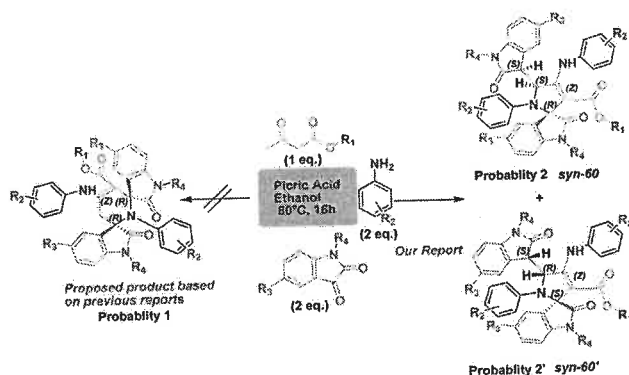
The spiro[indole-3,2'-pyrrole] framework was new and had a diverse scope of variations with different types of substituted isatins, arylamines and β -keto esters. Further, to the best of our knowledge and reviewing the recent reports, the MCR with arylamines, isatins and β -keto esters in ethanol using wet picric acid as the catalyst has not been documented to date. The use of β -keto esters in place of acetone increases the molecular diversity and also controls the formation of the conformational isomers of *syn*-60, while only one diastereomer has been reported^{24–26} for acetone based MCRs. Additionally, in

our structure we have three chiral centres C-3, C-4 and C-14 (Fig. 3) and theoretically there was a possibility of formation of 2^3 = 8 diastereomers along with other conformers around the hindered single bond.²⁷ Instead, under our experimental conditions two sets of diastereomers were isolated *syn*-60 (racemate- S^*S^*/R^*R^*) and *syn*-60' (racemate- S^*R^*/R^*S^*). Another possibility of *syn*-60'' (S^*S^*/R^*R^*) was arbitrarily chosen for DFT calculations to elucidate the relative ground state energies of *syn*-60, *syn*-60' and *syn*-60'' diastereomers of product 1h (entry 8, Table 2). We have assigned '60' to the conformers on the basis of the dihedral angle around the atoms H4-C4-C14-H14 (Fig. 3) being in the range of $\sim 60^\circ$ – 70° based on X-ray structures. Also ' S^* ' and ' R^* ' were assigned to *syn*-60 and *syn*-60' to show the relative but not the absolute configuration of multiple stereogenic centers (C-14, C-4 and C-3, Fig. 3) in the diastereomers. Thus, by evaluating the above reports, herein, we wish to present a straightforward, efficient, high-yielding and environmentally friendly one-pot multi-component reaction protocol for the synthesis of a series of densely functionalized tetrahydrospiro[indole-3,2'-pyrrole] derivatives and the factors affecting the formation of *syn*-60 and *syn*-60' isomers, using various electronic and steric groups in each of the components of the reactions. Further, DFT studies for the energy minimized state were carried out to support other characterization data *viz.* HMBC, HSQC, NOE NMR experiments, X-ray single crystallographic analysis and were in agreement with our experimental results that *syn*-60 was the most stable conformer that was isolated in all the reactions performed.

Results and discussion

Our investigation began on the basis of the previous report²⁸ with the reaction of ethylacetoacetate (1 mmol), isatin (2 mmol) and aniline (2 mmol) in the presence of wet picric acid (10 mol%) in MeOH : H₂O (6 : 4 v/v) at 0 °C to room temperature and by stirring for 16 h.

Crude LCMS showed the presence of intermediates while at 80 °C, the desired product was isolated in a very low yield (entries 9 & 10, Table 1). The said reaction was tested in various solvents *viz.* dichloromethane, acetonitrile, methanol-water, DMSO, THF and ethanol. The use of ethanol gave the best result where reactions at low and room temperature afforded the corresponding intermediates and at 80 °C, the desired products were formed in moderate to good yields (entries 11 & 12, Table 1). Further, there was no improvement in the reaction yield (75%) with increasing the reaction temperature and the amount of the catalyst from 10 to 20 mol% (entries 13, 14 and 15, Table 1). Also the reaction was idle in the absence of wet picric acid either under solvent-free conditions or in ethanol (entries 1 and 16, Table 1). Additionally, to evaluate the advantage of our catalytic system, a comparative study among several catalytic systems for the reaction was performed but in almost all cases we ended up in either poor yield or messy reaction profiles (entries 2–8 and 17–20, Table 1). As such, we empha-



Scheme 1 One-pot methodology for the synthesis of highly-functionalized spiro[indole-3,2'-pyrrole].



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Collaborative research in synthetic and structural organic chemistry
Number 27

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Period of Investigation: 01-10-2017 to 31-10-2018

Project: Transition Metal Nano Catalyst and Green Synthesis

Output: The result was published in the journal of international repute

**Publication: Utility of the Ditopic Nature of Magnetically Recyclable
NiFe₂O₄ Nano Catalyst for the Green Synthesis of Two Different
Spiro[indolinepyrrolizine] Scaffolds**

Soumyadip Basu, Utpal Kayal, Suwendu Maity, Prasanta Ghosh, Asim Bhaumik,
and Chhanda Mukhopadhyay

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Catalysis

Utility of the Ditopic Nature of Magnetically Recyclable NiFe_2O_4 Nano-Catalyst for the Green Synthesis of Two Different Spiro[indoline-pyrrolizine] ScaffoldsSoumyadip Basu,^[a] Utpal Kayal,^[b] Suwendu Maity,^[c] Prasanta Ghosh,^[c] Asim Bhaumik,^[b] and Chhanda Mukhopadhyay^{*[a]}

Environmentally benign and highly stable magnetic nano powder of NiFe_2O_4 was synthesized and characterized by XRD, HRTEM, EDX and Nitrogen BET adsorption isotherm analysis. Also, XPS analysis confirmed the electronic environment as well as the oxidation state of the elements. The NiFe_2O_4 catalyst was exploited in one-pot three-component synthesis of spiro[indoline-3,3'-pyrrolizine] and spiro[indoline-3,5'-pyrrolo[1,2-c]thiazole] scaffolds, because of its ditopic nature which can provide

both acidic (Fe^{3+}) and basic (O^{2-}) properties, require for the reactions. The desirability of this methodology resides in its simplicity, environmental friendliness, cost effectiveness and easier scaling up for bulk synthesis. Water was utilised as a medium for synthesis of the catalyst as well as the medium of the reaction leading to the product. The synthesized NiFe_2O_4 nanocatalyst can be recycled upto six times without any significant loss of activity.

Introduction

In modern science, nanotechnology and green chemistry^[1] are two simultaneous key factors in maintaining a sustainable eco-friendly society. In last few years, one of the most valuable fields in nanotechnology is Nanocatalysis.^[2] As catalysis is very important factor in various chemical protocols, nanocatalysis has drawn much attention in the development of green and pollution abatement processes. Nanocatalysis gives us various advantages in terms of the green aspects in many organic syntheses. It offers much simpler, environment friendly and economically efficient synthetic routes leading to the formation of the most desired product in maximum yield with easy separation and reusability of the catalyst.^[3] Nano catalysts by virtue of its very small size have high exposed surface area of its active component and thereby dramatically enhances the effective contact between the catalyst and reactants.^[4] Again, the insolubility of the Nano catalysts in the reaction solvents offers easy separation of the catalyst from the reaction mixture, which in turn results in effortless isolation of the product. Recently, Mixed metal oxide nanoparticles (MMONs) as nanocatalysts attracts interest among the chemists, and have

emerged as valuable alternatives in the development of various fields of modern organic transformations^[5] and greener reaction protocols.^[6] Notably, the MMONs exhibit much better catalytic activity and superior selectivity in various organic transformations compared to the individual oxides due to their increased surface area along with their enhanced active acidic and basic sites,^[7] which decreases the reaction time as well as enhance the yield of reactions^[8]. Thus, in the aspect of modern catalysis science, one of the most important and widely employed materials in organic chemistry in recent time is MMONs.

Nanocrystalline spinel metal ferrites with their general formula MFe_2O_4 (where, M = divalent metal ion,) have achieved a good amount of attention due to their several applications in different parts of science.^[9] Among these, NiFe_2O_4 , due to its high electrochemical stability, typical ferromagnetic properties and catalytic behaviour, emerges as one of the attractive ferrite because of its versatile application towards various fields such as biomedicine^[10] catalysts,^[11] ferrofluids,^[12] gas sensors^[13] and so on.^[14] Nickel ferrite, being a ferromagnetic oxide, has a typical inverse spinel cubic structure, where the Ni^{2+} ions occupy the octahedral sites and the ferric ions are equally distributed among the remaining octahedral and tetrahedral sites.^[15] Nano-range NiFe_2O_4 have been synthesized successfully by various methods including sol-gel,^[16] solid-state reaction,^[17] co-precipitation,^[18] combustion,^[19] micromulsion,^[20] thermolysis of mixed metal-oleate complexes,^[21] hydrothermal^[22] and sonochemical.^[23] We synthesize Nano-scale Nickel ferrite in a known method and study its catalytic application in the multicomponent synthesis of spiro[indoline-3,3'-pyrrolizine] and spiro[indoline-3,5'-pyrrolo[1,2-c]thiazol] scaffolds. Indeed, no previous work was reported for the synthesis of the above moieties using mixed metal oxide nanoparticles. Mixing a metal oxide catalyst with another metal oxide, causes in a critical

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interaction between two metal ions, which has high effect on chemical behaviour of the active sites and the catalytic performance of the mixed metal ions can be attuned. In our case, Fe_2O_3 enjoys a Lewis acidic character and whereas nickel oxide possesses a basic character but mixing of both to form a spinel (NiFe_2O_4) results the formation of new active sites with enhanced acidic and basic character. This dual catalytic behaviour makes NiFe_2O_4 nanoparticles very effective for use in MCRs as a heterogeneous "E" catalyst (Economic, Eco-friendly and Efficient). Again, due to its magnetic property, NiFe_2O_4 can be magnetically separable from the reaction mixture without much difficulty.

Multicomponent reactions (MCRs) with generation of lone product from numbers of starting materials in a single step provide a strategic importance for the construction of structurally diverse drug-like molecules and natural products.^[24] It generally proceeds with higher atom economy and the involvement of nontoxic intermediates, establishing its importance for the environment beyond doubt.^[25] Multicomponent reactions are associated with high efficiency, simple work-up,^[26] facile execution and cost effectiveness,^[27] increase its exploitation further. The efficiency and eco-compatibility of MCRs are enhanced when a recyclable heterogeneous catalyst is conjugated with the multicomponent strategy.^[28] However development of multicomponent strategy in aqueous environments has received comparatively little attention^[29] till now, but can be one of the major aspect of MCRs in coming days due to the harmful effects of organic solvents in the atmosphere. In this regard, water, being nature's own reaction medium and also a nontoxic, non-hazardous, non-flammable, redox stable, easily available solvent,^[30] can be developed as a green solvent in multicomponent syntheses. Therefore, design of multicomponent reactions using recyclable heterogeneous catalyst and water as a medium of reaction, is of greater importance, especially in the areas of drug discovery and materials science.

The 1,3-dipolar cycloaddition reaction of azomethine ylides with multiple Carbon-Carbon bonds is a productive methodology for synthesis of complex pyrrolidines scaffolds from simple precursors.^[31] Particularly, synthesis of pyrrolidinyl-3-spiro-oxindoles, has gained considerable attention because of their high biological activities. The basic core of spiro-oxindoles is part of huge number of naturally occurring bioactive alkaloids and medicinally relevant molecules like spirotryptostatin A&B,^[32] (-) horsfiline,^[33] (+)-elacomine,^[34] MI-129,^[35] alstonisine^[36] etc. Also the spiro heterocyclic motifs due to their distinct biological properties such as potent rhino virus and polio 3 C-proteinase inhibitions and aldose reductase inhibitors, represent an important class of natural substances.^[37] Again, the presence of Sulfur atom in the core structure spread the domain of the biological properties of the compounds.

Results and Discussion

With the challenge to obtain an efficient and recyclable mixed metal oxide nanoparticle (MMON) catalyst with high selectivity, we try to prepare nickel ferrite nanosized catalyst with spinel structure, having dual catalytic active sites. After the successful

preparation of catalyst, we employed it for the synthesis of spiro[indoline-3,3'-pyrrolizine] and spiro[indoline-3,5'-pyrrolo [1,2-c]thiazole] scaffolds via the insitu formation of azomethine ylide by a decarboxylative condensation between isatin and L-proline under environment benevolent condition. We also try the similar reaction with L-4-Thiazolidinecarboxylic acid instead of L-proline using NiFe_2O_4 catalyst. In both the cases we got exceptional results. Again, To ensure the successful formation of the nickel ferrite nanopowder catalyst, we performed powdered X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), EDX with elemental analysis, N_2 -adsorption analysis and XPS-analysis for the characterization of the synthesized material.

Characterization of Nickel Ferrite:

XRD-analysis: XRD pattern of the catalyst annealed at 700 °C was shown in Figure 1. The pattern clearly depicts the

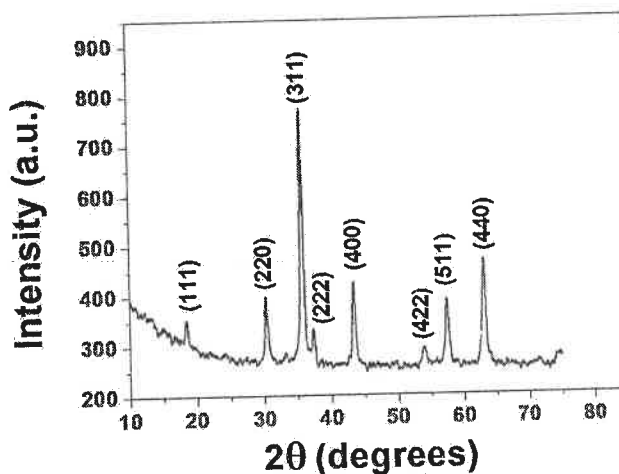


Figure 1. XRD Pattern of NiFe_2O_4 nanoparticles

formation of high quality polycrystalline nature single spinel phase of cubic NiFe_2O_4 . The appearance of diffraction peaks at (2θ values) 18.4, 30.3, 35.7, 37.3, 43.4, 53.8, 57.4 and 63.0 are the corresponding peaks for the reflection plane (111), (220), (311), (222), (400), (422), (511) and (440) respectively. Most intense diffraction peak for this face-centred cubic structure was observed at $2\theta = 35.7$ degree for the 311 plane. Other major intensity peaks also matches well with the cubic NiFe_2O_4 as per JCPDS 86-2267. These characteristic peaks indicate the formation of cubic spinel structure. Unit cell parameter for this cubic structure was $a = 8.3138 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$ together with the unit cell volume = 574.644 \AA^3 , which is little smaller than the nanocrystalline NiFe_2O_4 of $a = 8.332 \text{ \AA}$ as reported in the JCPDS database.

For this nanocrystalline NiFe_2O_4 NPs we can measure the mean crystallite size from the powder XRD data. We have employed the Scherrer equation $\text{FWHM} = (0.9 \lambda) / (D \times \cos \theta)$, to estimate the crystallite size from the powder XRD data. Here



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45
Collaborative

**Collaborative research in coordination and material chemistry
Number 28**

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Concerned Faculty: Dr. Md.Hedayetullah Mir, Dept. of Chemistry
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Concerned Scholar: Dr. Suman Kundu, Dept. of Chemistry

Period of Investigation: 01-05-2015 to 30-09-2016

Project: Coordination Polymers and the CO₂ Sorption Properties

Output: The result was published in a journal of international repute

**Publication: Halogen...Halogen Interactions in the Supramolecular Assembly of
2D Coordination Polymers and the CO₂ Sorption Behavior**

**F. Ahmed, S. Roy, K. Naskar, C. Sinha, S. M. Alam, Suman Kundu, J. J.
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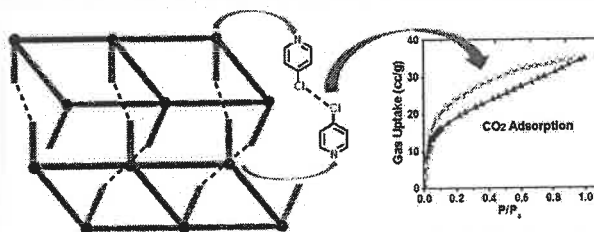
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Halogen...Halogen Interactions in the Supramolecular Assembly of 2D Coordination Polymers and the CO₂ Sorption BehaviorFaruk Ahmed,[†] Syamantak Roy,[‡] Kaushik Naskar,[§] Chittaranjan Sinha,[§] Seikh Mafiz Alam,[†] Suman Kundu,^{||} Jagadese J. Vittal,^{*,†,‡} and Mohammad Hedayetullah Mir^{*,†}[†]Department of Chemistry, Aliah University, New Town, Kolkata 700 156, India[‡]Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560 064, India[§]Department of Chemistry, Jadavpur University, Jadavpur, Kolkata 700 032, India^{||}Department of Chemistry, R. K. M. Residential College, Narendrapur, Kolkata 700 103, India^{*}Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117 543, Singapore

Supporting Information

ABSTRACT: Four new mixed-ligand divalent coordination polymers (CPs) [Cu₂(muco)₂(4-clpy)₂] (1), [Cu₂(muco)₂(4-brpy)₂] (2), [Zn₂(bdc)₂(4-clpy)₂] (3), and [Zn₂(bdc)₂(4-brpy)₂] (4) (H₂muco = *trans,trans*-muconic acid or 1,3-butadiene-1,4-dicarboxylic acid; H₂bdc = 1,4-benzene dicarboxylic acid; 4-clpy = 4-chloropyridine and 4-brpy = 4-bromopyridine) have been synthesized and well characterized by elemental analysis, infrared spectra, single-crystal X-ray diffraction techniques, powder X-ray diffraction patterns, and thermogravimetric analysis. All the compounds 1–4 have a two-dimensional (2D) coordination polymeric sheet structure. Of these, 1 and 2 are isotypical and form a 3D supramolecular aggregation based on type-I halogen–halogen interactions (Cl...Cl or Br...Br) and have an impact on CO₂ sorption properties. For the first time, halogen–halogen interactions have been used as a tool in the construction of high-dimensional CPs for sorption studies. However, analogous compounds 3 and 4 are expanded to 3D supramolecular structures based on π ... π interactions. These compounds have no halogen–halogen interactions and hence become nonporous toward CO₂ sorption. It appears that the halogen–halogen interactions between the 2D sheets are desirable for the uptake of CO₂ gas.



INTRODUCTION

Porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) have been extensively studied due to a great deal of interest as a new class of porous materials.^{1–5} The synthesis of PCPs has been particularly important due to their ability to systematically fine-tune the size and shape of the pore by choosing appropriate metal ions or metal clusters and suitable organic spacer ligands.^{6–8} PCPs are promising materials in gas storage and separation, ion exchange, trapping or sensing of target molecules, catalysis, magnetism, nonlinear optics, recognition, and sensing by enzymes in solution.^{9,10} Among these applications, the separation and purification of gases or vapors are of special interest.^{11,12} For example, selective adsorption of CO₂ gas is an important problem with respect to the greenhouse gas emission.¹³ Hence, researchers are interested in designing highly selective host frameworks to capture CO₂ and then release it more efficiently. Two-dimensional coordination polymers (2D CPs) have been employed not only to accommodate various guest molecules in the interlayer spaces^{14–16} but also for selective gas adsorption. It is possible to fine-tune the layer–layer interface by introducing weaker interactions, including H bonds, π –

electron stacking, and van der Waals interactions.^{17–19} Among the PCPs synthesized to date, only a few flexible structural motifs have been constructed by assembling the 2D layers via π – π stacking.^{20–22} The halogen–halogen interactions have been rarely used for this purpose.^{23–25}

Halogen–halogen interactions have become an increasingly popular field of research over the past decades for the construction of intriguing structures and prominent applications from catalysis to medicinal chemistry.^{26–32} Desiraju and co-workers have used this type of interaction for the design and crystal engineering of organic polymers.^{33,34} However, the utility of halogen–halogen interactions in the construction of high-dimensional PCPs for the sorption studies is still rare. Early reports have shown that halogen–halogen interactions play a major role in the assembly of high-dimensional supramolecular coordination polymers,^{23–25} but these interactions have not been used for the accommodation of guest species. Herein, we report four 2D CPs [Cu₂(muco)₂(4-clpy)₂]

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Table 1. Crystal Data and Refinement Parameters for Compounds 1–4

	1	2	3	4
formula	C ₂₂ H ₂₀ Cl ₂ Cu ₂ N ₂ O ₁₀	C ₂₂ H ₂₀ Br ₂ Cu ₂ N ₂ O ₁₀	C ₂₆ H ₁₆ Cl ₂ Zn ₂ N ₂ O ₈	C ₂₆ H ₁₆ Br ₂ Zn ₂ N ₂ O ₈
fw	670.38	759.30	686.05	774.97
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	C2/c	C2/c	P $\bar{1}$	P $\bar{1}$
a (Å)	21.046(4)	21.2857(13)	7.7201(2)	7.7138(4)
b (Å)	11.1739(17)	11.1539(6)	9.5991(3)	9.6730(5)
c (Å)	12.1686(19)	12.4229(8)	10.8117(3)	10.8188(5)
α (deg)	90	90	115.579(2)	115.805(2)
β (deg)	101.017(10)	102.565(4)	95.223(2)	94.506(2)
γ (deg)	90	90	102.942(2)	103.448(2)
V (Å ³)	2808.8(8)	2878.8(3)	688.08(4)	691.76(6)
Z	4	4	1	1
D _{calcd} (g/cm ³)	1.585	1.752	1.656	1.860
μ (mm ⁻¹)	1.758	4.306	1.989	4.673
λ (Å)	0.71073	0.71073	0.71073	0.71073
data [$I > 2\sigma(I)$]/params	3488/194	2549/194	2701/182	2667/182
GOF on F ²	1.098	1.049	1.067	1.001
final R indices [$I > 2\sigma(I)$] ^{a,b}	R1 = 0.0386 wR2 = 0.1137	R1 = 0.0313 wR2 = 0.0820	R1 = 0.0230 wR2 = 0.0593	R1 = 0.0412 wR2 = 0.1078

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, ^b wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2} \text{ on } w = 1/[\sigma^2 F_o^2 + (aP)^2 + bP], \text{ and } P = (F_o^2 + 2F_c^2)/3.$$

(1), [Cu₂(muco)₂(4-brpy)₂] (2), [Zn₂(bdc)₂(4-clpy)₂] (3), and [Zn₂(bdc)₂(4-brpy)₂] (4) (H₂muco = *trans,trans*-muconic acid or 1,3-butadiene-1,4-dicarboxylic acid; H₂bdc = 1,4-benzene dicarboxylic acid; 4-clpy = 4-chloropyridine and 4-brpy = 4-bromopyridine) assembled through weak interactions to form three-dimensional (3D) aggregates. Interestingly, compounds 1 and 2 exhibit the formation of 2D PCPs, which further undergo 3D supramolecular structures based on type-I halogen–halogen interactions (Cl⋯Cl or Br⋯Br), and these materials show CO₂ sorption properties. However, analogous compounds 3 and 4 do not have any halogen–halogen interactions and become nonporous toward CO₂ sorption. Therefore, it appears that the halogen–halogen interactions sustain the porosity of the coordination polymers and hence their sorption behavior.

EXPERIMENTAL SECTION

Materials and General Method. All chemicals purchased were reagent grade and were used without further purification. Elemental analysis (carbon, hydrogen, and nitrogen) was performed on a PerkinElmer 240C elemental analyzer. The infrared spectrum in KBr (4500–500 cm⁻¹) was recorded using a PerkinElmer FT-IR spectrum RX1 spectrometer. Thermogravimetric analyses were recorded on a PerkinElmer Pyris Diamond TG/DTA in the temperature range between 30 and 600 °C under a nitrogen atmosphere at a heating rate of 12 °C min⁻¹. The powder XRD data were collected on a Bruker D8 Advance X-ray diffractometer using Cu K α radiation (λ = 1.548 Å) generated at 40 kV and 40 mA. The PXRD spectrum was recorded in a 2 θ range of 5–50°.

Synthesis of Compounds 1–4. *Synthesis of Compound 1.* A solution of 4-clpy (0.030 g, 0.2 mmol) in MeOH (2 mL) was slowly and carefully layered to a solution of Cu(ClO₄)₂·6H₂O (0.074 g, 0.2 mmol), in H₂O (2 mL) using 2 mL of 1:1 (= v/v) buffer solution of MeOH and H₂O, followed by layering of H₂muco (0.028 g, 0.2 mmol) neutralizing with Et₃N (0.021 g, 0.2 mmol) in 2 mL of EtOH. The blue colored block crystals of [Cu₂(muco)₂(4-clpy)₂], 1, were obtained after 3 days (0.047 g, Yield 70%). Elemental analysis (%) calcd for C₂₂H₂₀Cl₂Cu₂N₂O₁₀: C 39.38, H 2.98, N 4.18; found: C 38.94, H 2.67, N 4.54. IR (KBr pellet, cm⁻¹): 1634 $\nu_{as}(\text{COO}^-)$, 1386 $\nu_{sym}(\text{COO}^-)$.

Compound 2. It was synthesized by a similar procedure as adopted for 1 using 4-brpy (0.039 g, 0.2 mmol) as auxiliary ligand instead of 4-

clpy. Blue block-shaped crystals [Cu₂(muco)₂(4-brpy)₂], 2, were obtained after a few days. (0.057 g, Yield 75%). Elemental analysis (%) calcd for C₂₂H₂₀Br₂Cu₂N₂O₁₀: C 34.76, H 2.63, N 3.68; found: C 34.57, H 2.35, N 3.96. IR (KBr pellet, cm⁻¹): 1634 $\nu_{as}(\text{COO}^-)$, 1385 $\nu_{sym}(\text{COO}^-)$.

Compound 3. It was synthesized by a similar procedure as adopted for 1 except using Zn(NO₃)₂·6H₂O (0.059 g, 0.2 mmol) instead of Cu(ClO₄)₂·6H₂O and H₂bdc (0.016 g, 0.2 mmol) instead of H₂muco. Colorless block-shaped crystals of [Zn₂(bdc)₂(4-clpy)₂], 3, were obtained after a few days. (0.055 g, Yield 80%). Elemental analysis (%) calcd for C₂₆H₁₆Cl₂Zn₂N₂O₈: C 45.50, H 2.33, N 4.08; found: C 45.52, H 2.35, N 4.20. IR (KBr pellet, cm⁻¹): 1638 $\nu_{as}(\text{COO}^-)$, 1393 $\nu_{sym}(\text{COO}^-)$.

Compound 4. It was synthesized by a similar procedure as adopted for 3 except using 4-brpy (0.039 g, 0.2 mmol) as auxiliary ligand instead of 4-clpy. Colorless block-shaped crystals of [Zn₂(bdc)₂(4-brpy)₂], 4, were obtained after a few days. (0.062 g, Yield 80%). Elemental analysis (%) calcd for C₂₆H₁₆Br₂Zn₂N₂O₈: C 40.28, H 2.06, N 3.62; found: C 40.20, H 2.16, N 3.38. IR (KBr pellet, cm⁻¹): 1645 $\nu_{as}(\text{COO}^-)$, 1387 $\nu_{sym}(\text{COO}^-)$.

Gas Adsorption Measurements. The adsorption isotherms of N₂ (77 K) and CO₂ (195 K) were measured using the dehydrated samples of 1 and 2 in a QUANTACHROME QUADRASORB-SI analyzer. In a sample tube, adsorbent samples 1 and 2 (~100–150 mg) were placed, which had been prepared at 120 °C, respectively, under 1 × 10⁻¹ Pa vacuum for about 6 h prior to measurement of the isotherms. Helium gas (99.999% purity) at a certain pressure was introduced in the gas chamber and allowed to diffuse into the sample chamber by opening the valve. The amount of gas adsorbed was calculated from the pressure difference ($P_{cal} - P_e$), where P_{cal} is the calculated pressure with no gas adsorption and P_e is the observed pressure at equilibrium. All operations were computer-controlled and automatic.

Water vapor adsorption was also measured at 298 K in the desolvated samples of 1 and 2 by using a BELSORP Aqua-3 analyzer. Around 80 mg of the samples was activated under similar conditions as mentioned earlier. Water molecules used to generate the vapor were fully degassed by repeated evacuation. The dead volume was measured with helium gas. The adsorbate was placed into the sample tube; then, the change in the pressure was monitored and the degree of adsorption was determined by the decrease in pressure at the equilibrium state. All operations were computer-controlled and automatic.



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Collaborative research in coordination and material chemistry
Number 29

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Concerned Scholar: Dr. Suman Kundu, Dept. of Chemistry

Period of Investigation: 01-10-2016 to 31-10-2017

Project: Coordination Polymers and their Applications

Output: The result was published in a journal of international repute

Publication: Cation dependent charge transport in linear dicarboxylate based
isotypical 1D coordination polymers
F. Ahmed, J. Datta, B. Dutta, K. Naskar, C. Sinha, S. M. Alam, Suman Kundu, P. P.
Ray and M. H. Mir
RSC Advances, 2017, 7, 10369-10375. <https://doi.org/10.1039/C7RA00165G>

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Cation dependent charge transport in linear dicarboxylate based isotypical 1D coordination polymers†

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Two new mixed-ligand one-dimensional coordination polymers (1D CPs) [Cd(adc)(4-phpy)₂(H₂O)₂], (1) and [Zn(adc)(4-phpy)₂(H₂O)₂], (2) (H₂adc = acetylenedicarboxylic acid and 4-phpy = 4-phenylpyridine) have been synthesized and well characterized by elemental analysis, infrared spectroscopy, single crystal X-ray diffraction, powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA). Both compounds 1 and 2 are isostructural and fabricate 3D supramolecular networks by the combination of hydrogen bonding and C–H... π interactions. Interestingly, these two materials exhibit electrical conductivity and reveal Schottky barrier diode behavior. To shed light on the charge transport mechanism of the compounds, the mobility, transit time, diffusion length and density of states at a quasi Fermi level have been derived. The analysis indicates that compound 1 has higher mobility ($9.15 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$) and diffusion length (1.116 μm) in comparison to compound 2 (mobility and diffusion length are $5.44 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 1.050 μm respectively). Compound 1, with the larger cation and shorter H-bonding distance, shows higher electrical conductivity, which is 2.55 times greater than compound 2.

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Introduction

Coordination polymers are inorganic–organic solid state materials containing metal ion centers or metal clusters linked by organic ligands extending in an array forming crystalline and highly ordered structures with high thermal stability.^{1–7} The design and synthesis of metal–organic coordination polymers or metal–organic frameworks (MOFs) have recently attracted immense interest, owing to their potential applications in gas storage,^{8–10} separation,^{11–14} magnetism,^{15–19} drug delivery,^{20–22} catalysis^{23–25} and sensing applications.^{26–28} Although it is a great challenge, by judicious choice of various ligands differing in lengths and functionalities, numerous MOFs with desired structures and properties have been obtained. However, utilization of MOFs in the fabrication of electronic devices is still at the age of infancy, because these materials exhibit low

electronic conductivity. Low conductivity of MOFs is a direct consequence of the engineering of these materials as they are typically constructed from hard metal ions linked by redox-inactive organic ligands, ensuing a poor conjugation pathway for charge transport.²⁹ Nevertheless, in the past few years, new approaches have been recognized for the construction of MOFs that exhibit high electrical conductivity.^{30–32}

A successful approach in the construction of thermodynamically stable coordination polymers is to utilize dicarboxylate ligands with rigid backbone that are capable of binding metal ions.^{33,34} These ligands would be good linear spacer and have been widely used due to their diverse coordination modes and bridging ability with metal ions. Recently, our group used linear dicarboxylate ligands to successfully synthesize a series of coordination polymers bonded through halogen–halogen interactions for the uptake of CO₂ gas.³⁵ Of various dicarboxylate ligands, utilization of acetylenedicarboxylate ([–]O₂CCCCO₂[–]) seems to be scarce in the literature.³⁶ Herein, we report two acetylenedicarboxylate based one-dimensional coordination polymers (1D CPs), [Cd(adc)(4-phpy)₂(H₂O)₂], (1) and [Zn(adc)(4-phpy)₂(H₂O)₂], (2) (H₂adc = acetylenedicarboxylic acid and 4-phpy = 4-phenylpyridine) assembled through weak interactions to form three-dimensional (3D) aggregates. Interestingly, these materials exhibit electrical conductivity of the order 10^{–7} S cm^{–1} which is in the range of semiconductor and reveal Schottky barrier diode behavior. However, conductivity and photosensitivity of 1 are enhanced in both dark and under

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† Electronic supplementary information (ESI) available: Fig. S1–S2, Tables S1–S5, TGA, PXRD, FTIR and X-ray crystallographic data in CIF format for compounds 1–2. CCDC 1517763 and 1517764. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7ra00165g



illumination because of the lesser band gap and increased charge transport due to the photon excitation. The mobility, diffusion length, density of states (DOS) at quasi Fermi level indicates the better charge transport for the device fabricated with **1**. In these materials, as the metal carboxylate chains are not expected to transport charge, the increase in conductivity of **1** is associated with increase in size of the ionic radii of the Cd^{2+} compared to Zn^{2+} .^{29,37} Besides, ionic radii and conductivity have been correlated with the simultaneous decrease in H-bonding distance among the adjacent layers in **1**. Indeed, the H-bonding distance decreases from 2.72 Å in **2** to 2.68 Å in **1**. Therefore, larger size of cation and shorter H-bonding distance among the layers lead to the higher electrical conductivity in compound **1**. Electrical conductivity of **1** is 2.55 times greater than **2**. Mobility of compound **1** is also enhanced by 68% compared to **2**.

Experimental section

Materials and physical method

The all chemicals purchased were reagent grade and were used without further purification. Elemental analysis (carbon, hydrogen and nitrogen) was performed on a Perkin-Elmer 240C elemental analyzer. Infrared spectrum in KBr (4500–500 cm^{-1}) was recorded using a Perkin-Elmer FT-IR spectrum RX1 spectrometer. Thermogravimetric analyses were recorded on a Perkin-Elmer Pyris Diamond TG/DTA in the temperature range 30–600 °C under a nitrogen atmosphere. The powder XRD data was collected on a Bruker D8 Advance X-ray diffractometer using Cu K α radiation ($\lambda = 1.548$ Å) generated at 40 kV and 40 mA. The PXRD spectrum was recorded in a 2θ range of 5–50. Solid state electronic absorption spectra were recorded on a PerkinElmer UV/VIS Spectrophotometer (LAMBDA 35). Solid state emission spectra were recorded on a HORIBA Jobin Yvon (Fluoromax-4) fluorescence spectrophotometer. The optical characterization was studied with the help of Shimadzu 2401 PC UV-vis spectrophotometer, in the range of 250–800 nm. Electrochemical impedance spectroscopy (EIS) study is done by Agilent 4295A LCR instrument.

Synthesis of compounds **1** and **2**

Synthesis of compound 1. A solution of 4-pphy (31 mg, 0.2 mmol) in MeOH (2 mL) was slowly and carefully layered to a solution of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (62 mg, 0.2 mmol), in H_2O (2 mL) using 2 mL 1 : 1 (=v/v) buffer solution of MeOH and H_2O followed by layering of H_2adc (23 mg, 0.2 mmol) neutralized with Et_3N (0.027 mL, 0.2 mmol) in 2 mL EtOH. The colorless block crystals of $[\text{Cd}(\text{adc})(4\text{-pphy})_2(\text{H}_2\text{O})_2]$, **1** were obtained after three days (69 mg, yield 60%). Elemental analysis (%) calcd for $\text{C}_{26}\text{H}_{22}\text{CdN}_2\text{O}_6$: C 54.65, H 3.85, N 4.90; found: C 54.95, H 3.67, N 4.54. IR (KBr pellet, cm^{-1}): 1592 $\nu_{\text{as}}(\text{COO}^-)$, 1317 $\nu_{\text{sym}}(\text{COO}^-)$.

Compound 2. It was synthesized by a similar procedure as adopted for **1** except using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (60 mg, 0.2 mmol). Colorless block shaped crystals $[\text{Zn}(\text{adc})(4\text{-pphy})_2(\text{H}_2\text{O})_2]$, **2** were obtained after few days. (68 mg, yield 65%). Elemental analysis (%) calcd for $\text{C}_{26}\text{H}_{22}\text{ZnN}_2\text{O}_6$: 59.40, H 4.20, N 5.35; found: C

59.57, H 4.15, N 5.56. IR (KBr pellet, cm^{-1}): 1590 $\nu_{\text{as}}(\text{COO}^-)$, 1322 $\nu_{\text{sym}}(\text{COO}^-)$.

General X-ray crystallography

Single crystal of the compound **1** and **2** having suitable dimensions, was used for data collection using a Bruker SMART APEX II diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The molecular structure was solved using the SHELX-97 package.³⁸ Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. The crystallographic data for **1** and **2** are summarized in Table S1† and selected bond lengths and bond angles are given in Tables S2 and S3.†

Device fabrication and characterization

To fabricate the Schottky device, at first, indium tin oxide (ITO) coated glass substrate was cleaned in isopropanol and ultrasonicated in a bath for 15 min. Then it was further cleaned in acetone and de-ionized water sequentially. This cleaned ITO coated glass was dried in vacuum chamber. At the same time well dispersed solutions of the sample **1** and **2** in the dimethyl sulfoxide (DMSO) medium were prepared and spin coated onto the dried ITO glass at 400 rpm for 1 min with the help of SCU 2700 spin coating unit. This spin coating step was repeated for 4 times. After drying in vacuum, the film thickness was measured as 10 μm by surface profiler. At the last step of fabrication, aluminum (Al) electrodes were deposited onto the film by a Vacuum Coating Unit 12A4D of HINDHIVAC under pressure 10^{-6} Torr. The area of the Al electrodes was maintained as $7.065 \times 10^{-6} \text{ m}^2$ by the shadow mask. Current–voltage measurements of the fabricated device were done by a Keithley 2400 source meter by two-probe technique under dark and illumination at room temperature.

Electrical characterization

To study the current–voltage (I – V) characteristics, two devices of Al/compound **1**/ITO (Device-a) and Al/compound **2**/ITO (Device-b) were fabricated. A bias voltage varying from –6 V to +6 V was applied to the devices at room temperature under dark and light condition. The structure of Device-a (or Device-b) is shown on Fig. S1† including the direction of light.

Results and discussion

Structural descriptions of $[\text{Cd}(\text{adc})(4\text{-pphy})_2(\text{H}_2\text{O})_2]$, (**1**) and $[\text{Zn}(\text{adc})(4\text{-pphy})_2(\text{H}_2\text{O})_2]$, (**2**)

Single crystal X-ray crystallography revealed that both **1** and **2** are isotypical. However, compound **1** crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$. Asymmetric unit in **1** contains distorted octahedral $\text{Cd}(\text{II})$ centre ligated by two O atoms from two adc anions in monodentate fashion (Cd–O, 2.289(3)–2.292(3) Å) and two N atoms from two 4-pphy ligands (Cd–N, 2.339(4)–2.343(5) Å) in the equatorial plane, and by O atoms from two aqua ligands at the axial sites (Cd–O, 2.301(3)–2.306(3) Å)





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Collaborative research in coordination and material chemistry
Number 30

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Institute 2: Ramakrishna Mission Residential College (Autonomous)

Concerned Scholar: Dr. Suman Kundu, Dept. of Chemistry

Period of Investigation: 01-10-2016 to 31-10-2017

Project: Coordination Polymers and their Applications

Output: The result was published in a journal of international repute

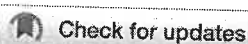
**Publication: Synthesis and structural characterization of a Cu(II)-based
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**F. Ahmed, S. Halder, B. Dutta, S. Islam, C. Sen, Suman Kundu, C. Sinha, P. P. Ray
and M. H. Mir**

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Dr. Md. Hedayetullah Mir

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Synthesis and structural characterization of a Cu(II)-based 1D coordination polymer and its application in Schottky devices†

Faruk Ahmed,^a Soumi Halder,^b Basudeb Dutta,^a Sakhiul Islam,^a Chandana Sen,^c
Suman Kundu,^d Chittaranjan Sinha,^e Partha Pratim Ray^e*^b and
Mohammad Hedayetullah Mir^e*^a

A new Cu(II) based one-dimensional coordination polymer (1D CP), [Cu(fum)(4-phpy)₂(H₂O)] (**1**) (H₂fum = fumaric acid and 4-phpy = 4-phenyl pyridine), has been synthesized and well characterized using elemental analysis, infrared spectra, single crystal X-ray diffraction (SCXRD) techniques, powder X-ray diffraction (PXRD) patterns, scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). In the solid state structure, 1D chains are self-assembled through strong intermolecular hydrogen bonding to give a 2D sheet structure. These 2D sheets are further accumulated to fabricate 3D supramolecular aggregates via weak CH... π interactions. The band gap measurement which is equivalent to the HOMO–LUMO gap calculated by density functional theory (DFT) computations confirms the semiconducting properties of the material. To gain insight into the charge transport mechanism of the compound, its mobility, lifetime and diffusion length have been estimated. The analysis indicates that compound **1** may be applied in active electronic devices. Finally, a metal–CP junction Schottky barrier diode has been successfully fabricated and studied in detail.

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Introduction

In the last few decades, coordination polymers (CPs) have attracted a great deal of interest in the field of solid state chemistry.^{1–9} In particular, porous coordination polymers (PCPs) or metal–organic frameworks (MOFs) have attracted special interest due to their wide spectrum of applications in gas storage and separation,^{10–16} ion exchange,^{17,18} recognition,^{19,20} magnetism,^{21–25} drug delivery,^{26–28} catalysis,^{29–31} and seizure or sensing of target molecules.^{32–36} The interesting feature of coordination polymers is the possibility of an infinite number of structural diversities by varying various ligands differing in lengths and functionalities. Depending on the endless structural variety of CPs, various new

fields like nonlinear optics, Schottky diodes and energy storage devices have recently emerged.^{37–41} However, it is observed that a few number of CPs have been characterized with conductive properties with some specially chosen organic ligands. Therefore, the challenges lie in designing organic linkers and controlling the supramolecular assembly within the framework for the conjugation pathway for charge transport.⁴²

Dicarboxylic acids are multidentate ligands, which generate very rich coordination chemistry.⁶ Dicarboxylate and nitrogen based bidentate linkers have been extensively used for the construction of desired higher dimensional CPs.⁷ However, the use of monodentate nitrogen donor ligands seems to be not much known in the literature. Our aim is to develop CPs made of metal ions and bidentate dicarboxylate ligands and additional monodentate linkers (e.g. pyridine based ligands) will be in the perpendicular direction.⁴³ Here, monodentate nitrogen donors will be used to look into the role of supramolecular interaction in crystal engineering. Recently, our group has synthesized two one-dimensional (1D) CPs bonded through weak interactions to construct higher dimensional supramolecular aggregates and capable of behaving as Schottky devices.⁴⁴

In continuation of our previous work, for better performance of the device, we have changed the metal centre by adopting Cu(II), keeping the redox inactive ligand system almost the same. Here we report a fumarate based 1D CP, [Cu(fum)(4-phpy)₂(H₂O)] (**1**)

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† Electronic supplementary information (ESI) available: Fig. S1, Tables S1–S4, TGA, PXRD, FESEM image and X-ray crystallographic data in CIF format for compound **1**. CCDC 1532657. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7nj01557g

(H₂fum = fumaric acid and 4-phpy = 4-phenyl pyridine), using a pyridyl co-ligand, which forms 3D supramolecular aggregates by combination of hydrogen bonding and CH $\cdots\pi$ interactions. This material exhibits better electrical conductivity and charge transport properties for application in active devices. However, it remains always a technological challenge to apply this material in active electronic devices. We have successfully been able to apply this material in a metal-CP Schottky diode and analyzed the performance of the device in detail. To the best of our knowledge, the application of Cu(II) based CPs in Schottky barrier diodes seems to be rarely reported in the literature. Here, enhanced conductivity from our previously reported materials may be due to the presence of square-pyramidal d⁹ Cu(II) centers possessing loosely bound electrons.^{42,45}

Experimental section

Materials and physical method

All chemicals purchased were of reagent grade and were used without further purification. Elemental analysis (carbon, hydrogen and nitrogen) was performed on a Perkin-Elmer 240C elemental analyzer. An infrared spectrum in KBr (4500–500 cm⁻¹) was recorded using a Perkin-Elmer FT-IR spectrum RX1 spectrometer. Thermogravimetric analysis was performed using a Perkin-Elmer Pyris Diamond TG/DTA in the 30 °C and 600 °C temperature range under a nitrogen atmosphere at a heating rate of 12 °C min⁻¹. The powder XRD data were collected on a Bruker D8 Advance X-ray diffractometer using Cu K α radiation (λ = 1.548 Å) generated at 40 kV and 40 mA. The PXRD spectrum was recorded in the 5–50° 2 θ range. The structural characterisation of the synthesized material was carried out using an FEI make Inspect F50 field emission scanning electron microscope (FESEM). The electrical characterization was performed with the help of a Keithley 2400 sourcemeter, interfaced with a PC.

Synthesis of compound 1

A solution of 4-phpy (0.031 g, 0.2 mmol) in MeOH (2 mL) was slowly and carefully layered on a solution of Cu(NO₃)₂·3H₂O (0.048 g, 0.2 mmol) in H₂O (2 mL) using 2 mL of a 1 : 1 (= v/v) buffer solution of MeOH and H₂O followed by layering of H₂fum (0.023 g, 0.2 mmol) neutralized with Et₃N (0.021 g, 0.2 mmol) in 2 mL of EtOH. Block shaped blue crystals of [Cu(fum)(4-phpy)₂(H₂O)], **1**, were obtained after three days (0.071 g, yield 70%). Elemental analysis (%) calcd for C₂₆H₂₂CuN₂O₅: C 61.66, H 4.35, N 5.53; found: C 61.94, H 4.67, N 5.64. IR (KBr pellet, cm⁻¹): 1595 $\nu_{\text{as}}(\text{COO}^-)$, 1370 $\nu_{\text{sym}}(\text{COO}^-)$.

General X-ray crystallography

Single crystals of compound **1** having suitable dimensions were used for data collection using a Bruker SMART APEX II diffractometer equipped with a graphite-monochromated MoK α radiation source (λ = 0.71073 Å). The molecular structure was solved using the SHELX-97 package.⁴⁶ Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically idealized positions and constrained to

ride on their parent atoms. The crystallographic data for **1** are summarized in Table S1 (ESI†) and selected bond lengths and bond angles are given in Table S2 (ESI†).

Device fabrication and characterization

Prior to device fabrication an ITO coated glass substrate was cleaned using an ultrasonication method in ethanol, acetone and distilled water for 15 min followed by drying of the substrate. A thin film of the synthesised material was obtained by spin coating the well dispersed solution of the material at 400 rpm for 2 min. Then it was dried in a vacuum oven at 90 °C. Finally, aluminium (Al) electrodes were deposited on the film using a Vacuum Coating Unit 12A4D of HINDVAC. The current-voltage measurements were performed by using a Keithley 2400 source meter in the ± 1 V range. Optical characterization of the material was done using a Shimadzu 2401 PC UV-Vis spectrophotometer. A well dispersed solution of the material was prepared in DMF solution and the absorption spectrum of the material was recorded in the 200–900 nm wavelength range.

Computational study

All calculations were carried out at the B3LYP^{47,48} level using Gaussian 09 software.⁴⁹ The LanL2DZ basis set was assigned for the elements. All the ground state stationary points were fully optimized at the B3LYP/LanL2DZ level.⁵⁰ Vertical electronic excitations based on B3LYP optimized geometries were computed using the time-dependent density functional theory (TDDFT) formalism^{51,52} in methanol using the conductor-like polarizable continuum model (CPCM).^{53,54}

Results and discussion

Structural description of [Cu(fum)(4-phpy)₂(H₂O)], (**1**)

Single crystal X-ray crystallography revealed that compound **1** crystallizes in the orthorhombic space group *P*2₁2₁2₁ with *Z* = 4. The Cu(II) centre in **1** has a square pyramidal coordination environment ligated by two O atoms from two fum anions in a monodentate fashion (Cu–O, 1.916(2)–1.925(2) Å) and two N atoms from two 4-phpy ligands (Cu–N, 2.039(3)–2.042(3) Å) in the equatorial plane, and by an oxygen atom from one aqua ligand at the apical position (Cu–O, 2.204(3) Å) (Fig. 1a). The connectivity of the neighboring carboxylate oxygen atoms with Cu(II) centers results in a 1D coordination polymer (Fig. 1b). In the solid state structure, these 1D chains are self-assembled through strong intermolecular H-bonding with O \cdots O separations of 2.68–2.69 Å between the aqua ligands and the O atom of the bridging fum ligands (Fig. 1c) to fabricate a two dimensional (2D) aggregate. These 2D hydrogen bonded planes undergo edge to face weak C–H $\cdots\pi$ interactions (3.234–3.502 Å) to construct a 3D supramolecular network (Fig. S1, ESI†).

TGA, PXRD and FESEM study

To check the thermal stability of the compound, thermogravimetric analysis (TGA) was performed with a fresh sample within the 30 °C to 600 °C temperature range under a N₂ atmosphere. The result



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Collaborative research in coordination and material chemistry

Number 31

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Period of Investigation: 01-09-2016 to 30-09-2017

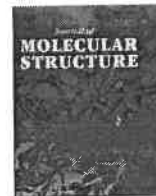
Project: Transition Metal Schiff Base Complexes

Output: The result was published in a journal of international repute

Publication: Copper(II) and palladium(II) complexes with tridentate NSO donor
Schiff base ligand: Synthesis, characterization and structures
Sujit Baran Kumar, Ankita Solanki, Suman Kundu
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<https://doi.org/10.1016/j.molstruc.2017.04.081>

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Copper(II) and palladium(II) complexes with tridentate NSO donor Schiff base ligand: Synthesis, characterization and structures



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ABSTRACT

Mononuclear copper(II) complex [CuL₂] and palladium(II) complexes [Pd(X)L] where X = benzoate(bz) or salicylate(sal) and HL = 2-(methylthio)phenylimino)methyl)phenol, a Schiff base ligand with NSO coordination sites have been synthesized and characterized by microanalyses, IR, UV–Visible spectra, conductivity measurement and magnetic studies. Crystal structures of all the complexes have been solved by single crystal X-ray diffraction studies and showed that there are two molecules in a unit cell in the [CuL₂] complex - one molecule has square planar geometry whereas second molecule has distorted square pyramidal geometry and palladium(II) complexes have distorted square planar geometry.

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1. Introduction

Schiff bases have been used as versatile chelating ligand in the synthesis of transition metal complexes because of their ease of preparation and structural variation. Schiff base containing transition metal complexes have been investigated extensively because they have wide application in the fields of biology and catalysis [1–10]. Metal complexes with Schiff base containing N and O donor atoms derived from aromatic amine and salicylaldehyde have been studied extensively and there are many compounds reported in the literature. Transition metal complexes with Schiff base chelating ligand containing hetero N, S and O donor atoms are very interesting because compounds with NSO donor atoms have biological and catalytic activity and there are many reports on the catalytic and bioactivity of metal complexes with NSO coordinate ligand [11–17]. There has been considerable interest in palladium complexes with Schiff base ligand because of their potential catalytic and biological activity [18–23]. As properties of the metal complexes depend on the coordination environment around the metal centre, we are interested to see the coordination behaviour of NSO donor ligand in the copper(II) and palladium(II) complexes.

In this paper, we report on the synthesis, characterization and

structures of mononuclear copper(II) complex [CuL₂] and palladium(II) complexes of the type [Pd(X)L] where HL = 2-(methylthio)phenylimino)methyl)phenol, a tridentate N, S and O donor atoms containing ligand and X = benzoate or salicylate.

2. Experimental

2.1. Materials

All chemicals and solvents used were analytical grade reagents. 2-Methylthioaniline, Pd(CH₃COO)₂ (Aldrich) and salicylaldehyde (Loba) were reagent grade and used as received. 2-(methylthio)phenylimino)methyl)phenol (HL) was synthesized by refluxing the mixture of 2-methylthioaniline and salicylaldehyde in ethanol. Cu(ClO₄)₂·6H₂O was prepared by reaction of cupric carbonate with dilute HClO₄ acid, followed by slow evaporation of the solution.

2.2. Instruments

The micro analysis (C, H and N) were carried out using a Perkin-Elmer IA 2400 series elemental analyzer. The IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer RX1 spectrum using KBr pellets. UV–Vis spectra (1200–190 nm) were recorded on a Shimadzu 3600 in CH₃CN solution. Solution conductivity were measured in CH₃CN solution using Equip-Tronics conductivity

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meter (model no. EQ-660A). Room temperature magnetic susceptibility of powder sample was measured by Guoy balance.

2.3. Syntheses of complexes

2.3.1. Synthesis of complex [CuL₂] (1)

A methanol solution (10 mL) of ligand HL (0.244 g, 1.0 mmol) was added drop wise to a stirring methanol solution (10 mL) of Cu(ClO₄)₂·6H₂O (0.185 g, 0.5 mmol) and stirring was continued for 3 h. The solution was filtered and the filtrate was kept for slow evaporation. Dark green coloured crystals were obtained from the filtrate after 5 days.

Yield. (0.160 g, 50%). Found. C = 61.68, H = 4.40, N = 5.12%. Anal calc for C₂₈H₂₄N₂CuO₂S₂: C = 61.36, H = 4.38, N = 5.11%. IR (KBr pellet) cm⁻¹; ν (C = N) 1604 s. UV–Vis spectra: λ_{max} /nm (ϵ_{max} /mol⁻¹cm⁻¹). 679(127). 398(5969), 231(25563), Δ_M (Ω^{-1} cm² mol⁻¹) = 14. μ_{eff} = 1.80 BM.

2.3.2. Synthesis of complex [Pd(bz)L] (2)

A solution of ligand HL (0.061 g, 0.25 mmol) in acetonitrile (10 ml) was added drop by drop to an acetonitrile solution (10 mL) of Pd(CH₃COO)₂ (0.056 g, 0.25 mmol) with stirring. To this, a solution of benzoic acid (0.25 mmol) in acetonitrile (10 mL) was added and stirring was continued for 3 h. Filtered the solution and the solution was kept for slow evaporation. Orange coloured crystals were obtained from the solution after 5 days. Yield. 0.075 g (63%). Found C = 53.70, H = 3.60, N = 2.90%. Anal calc for C₂₁H₁₇NO₃PdS; C = 53.68, H = 3.62, N = 2.98%. IR (KBr pellet) cm⁻¹; ν (C=N), 1606s; ν (Pd–N), 479. UV–Vis spectra: λ_{max} /nm(ϵ_{max} /mol⁻¹cm⁻¹). 447(7061), 317(14110), 242(35420).

2.3.3. Synthesis of complex [Pd(sal)L] (3)

The complex was synthesized by following the similar procedure to that of 2, but salicylic acid was used in place of benzoic acid. Yield. 0.082 g (67%). Found C = 51.93, H = 3.55, N = 2.78%. Anal calc for C₂₁H₁₈NO₄PdS; C = 51.87, H = 3.70, N = 2.88%. IR (KBr pellet) cm⁻¹; ν (C=N), 1607s; ν (Pd–N), 479. UV–Vis spectra. λ_{max} /nm(ϵ_{max} /mol⁻¹cm⁻¹). 446 (6077), 318 (11812), 227 (35590).

2.4. X-ray crystallography

Crystals for X-ray diffraction of the compounds 1, 2 and 3 were obtained through slow evaporation of the solution. Single crystal X-ray diffraction intensity measurements were performed on Oxford X-CALIBUR-S diffractometer equipped with CCD detector using Mo-K α radiation (λ = 0.71073 Å) for complex 1 and Cu-K α radiation (λ = 1.54184 Å) for complexes 2 and 3. The reflection were measured in the range of 3.71–28.09° for complex 1, 4.68–88.79° for complex 2 and 4.065–73.03° for complex 3. Data reduction was carried out using the program CrysAlisPro, Agilent Technologies, Version 1.171.35.19 [24]. An absorption correction based on multi-scan method was applied [25]. The structure was solved by direct methods and refinement was performed by the full-matrix least-square technique on F^2 using the programs SHELXS-97 and SHELXL-97 respectively [26]. All calculations were carried out using WinGX system Ver-1.64 [27]. All hydrogen atoms were located from difference Fourier map and treated as riding. All non-hydrogen atoms were refined with anisotropic displacement coefficients (See Table 1).

3. Results and discussion

3.1. Synthesis

Mononuclear copper(II) complex [CuL₂] was readily obtained

with good yield (~50%) by the reaction of Cu(ClO₄)₂·6H₂O with the ligand HL in 1:2 mol ratio in methanol at room temperature [Scheme 1]. The molecular composition of the complex was supported by micro analyses, IR and solution conductivity measurement. Molar conductivity measurement of the complex in CH₃CN solution (~10⁻³M) shows that the complex has very low molar conductivity (Δ_M ~10 Ω^{-1} cm² mol⁻¹), indicating the complex is neutral and no counter anion is present. Infrared spectrum of the complex also indicate the absence of ClO₄⁻ ion in the complex. Single crystal X-ray diffraction study of the copper(II) complex shows there are two molecules in the unit cell-one molecule has square planar geometry where the ligand acts as bidentate and another molecule has distorted square pyramidal geometry where one ligand acts as bidentate ligand with N,O coordination mode but another ligand acts as tridentate with N, S and O coordination mode. The structure and bioactivities of the ternary five coordinated copper(II) complexes with this NSO donor ligand and nitrogen containing heterocycle ligand is reported in the literature [11,28,29]. The complex is moderately soluble in organic solvents such as acetonitrile, methanol, ethanol, dichloromethane, acetone etc.

Mononuclear palladium(II) complexes of the type [Pd(X)L] were readily obtained in good yield (65%) by the reaction of Pd(CH₃COO)₂, ligand HL and HX (where HX = salicylic acid/benzoic acid) in 1:1:1 mol ratio in acetonitrile at room temperature. Orange coloured crystals of [Pd(X)L] were obtained by slow evaporation of acetonitrile solution of the complexes. Both the complexes have slightly distorted square planar geometry. The Schiff base ligand L acts as tridentate monoprotic NSO coordinate ligand in both the complexes. The microanalysis data of the two complexes are found to be consistent with their molecular compositions. There is no change in composition even after adding excess benzoic/salicylic acid. Molar conductivity measurements in CH₃CN solution show the complexes are neutral. The complexes are soluble in common organic solvents like dichloromethane, methanol, acetonitrile etc.

3.2. IR data

The IR spectra of the complexes were assigned by comparing the IR spectra of the ligand HL. The IR spectrum of all the complexes exhibit one strong band at 1604 cm⁻¹ correspond to ν (C=N) of imine and the absence of ligand's phenolic –OH band in the region of 3320 cm⁻¹ in the compounds confirming the coordination of phenolic-OH with metal centre in the complexes. Infrared spectra of both complexes 2 and 3 are nearly identical. For both the compounds, one weak band exhibited at 479 cm⁻¹ due to ν (Pd–N) [30] and one strong absorption band exhibited at 1376 and 1335 cm⁻¹ for the complexes 2 and 3 respectively, due to asymmetric stretching vibration of monodentate –COO⁻ group confirming the coordination of acid ligand with palladium(II) ions. For [Pd(sal)L], the phenolic-OH is not coordinated to the palladium centre and therefore, salicylic acid acts as monodentate ligand and coordinate only through oxygen atom of carboxylate ion. This was confirmed by single crystal X-ray diffraction study of the complex 3. This type of non-coordination of phenolic-OH group in the complexes was reported in the literature [31]. Finally, coordination of ligand with metal atoms were confirmed by single crystal X-ray diffraction studies.

3.3. UV–vis spectra

The UV–Vis spectra of both the complexes were recorded in the range of 200–1100 nm in CH₃CN. A broad absorption band observed at 679 nm with ϵ = ~131 mol⁻¹ cm⁻¹ for complex 1 which is attributed to d-d transition. For palladium(II) complexes, both the



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Collaborative research in coordination and material chemistry

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Chittaranjan Sinha

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Synthesis, characterisation, photochromic study of cadmium(II) halide complexes of 1-alkyl-2-methyl-4-(*p*-nitro-phenylazo)imidazole and DFT computation

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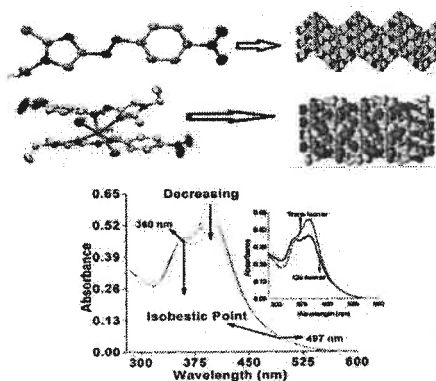
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1-Alkyl-2-methyl-4-(*p*-nitro-phenylazo)imidazole complexes of Cd(II), Cd[$\{p\text{-NO}_2\text{-aai(Me)R}\}_2\text{X}_2$] (2-4) [$\{p\text{-NO}_2\text{-aai(Me)R} = 1\text{-alkyl-2-methyl-4-(para-nitro-phenylazo)imidazole}\}$, {R = -CH₃ (1a), -C₂H₅ (1b)} (X = Cl, Br, I)] have been synthesized and characterized by spectral (UV-Vis, IR, ¹H NMR) data and have been confirmed by single crystal X-ray diffraction study in the case $p\text{-NO}_2\text{-aai(2-Me)1-C}_2\text{H}_5$ (1b) and Cd[$\{p\text{-NO}_2\text{-aai(2-Me)1-C}_2\text{H}_5\}_2\text{I}_2$] (4b). Both ligands and complexes undergo *E(trans)*-to-*Z(cis)* isomerization when irradiated with UV light. The reverse *Z(cis)*-to-*E(trans)* isomerization can be driven thermally in the dark. The rates and quantum yields ($\phi_{E \rightarrow Z}$) of *E*-to-*Z* isomerisation are higher for free ligand, 1, than their complexes, 2-4. The activation energies (E_a) and activation entropies (ΔS) of the *Z*-to-*E* isomerization are calculated by controlled temperature experiment (298–313 K). Effect of halides on the rate and quantum yields of photochromism is established and has been supported by DFT computation of optimized structures. Slow rate of photoisomerisation of coordinated ligands compare to the free ligands may be due to increased mass and rotor volume of the complexes. The rate of isomerization follows the sequence Cd[$\{p\text{-NO}_2\text{-aai(2-Me)1-C}_2\text{H}_5\}_2\text{Cl}_2$] < Cd[$\{p\text{-NO}_2\text{-aai(2-Me)1-C}_2\text{H}_5\}_2\text{Br}_2$] < Cd[$\{p\text{-NO}_2\text{-aai(2-Me)1-C}_2\text{H}_5\}_2\text{I}_2$].

Keywords: Cd(II) complexes, ligand, X-ray structures, photoisomerisation, DFT computation.



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Collaborative research in synthetic and structural inorganic chemistry
Number 33

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Institute 2: Ramakrishna Mission Residential College (Autonomous)

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**Publication: Exploring the effect of hydroxylic and non-hydroxylic solvents
on the reaction of $[V^{IV}O(\beta\text{-diketonate})_2]$ with 2-aminobenzoylhydrazide in
aerobic and anaerobic conditions**

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Exploring the effect of substituent in the hydrazone ligand of a family of μ -oxidodivanadium(v) hydrazone complexes on structure, DNA binding and anticancer activity†

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The reaction of 2-hydroxybenzoylhydrazine (H_2bh) separately with equimolar amounts of $[V^{IV}O(aa)_2]$ and $[V^{IV}O(ba)_2]$ in $CHCl_3$ afforded the complexes $[V_2O_3(HL^1)_2]$ (**1**) and $[V_2O_3(HL^2)_2]$ (**2**) respectively in good to excellent yield ($(HL^1)^{2-}$ and $(HL^2)^{2-}$ represent respectively the dianionic form of 2-hydroxybenzoylhydrazones of acetylacetone (H_3L^1) and benzoylacetone (H_3L^2) (general abbreviation H_3L)). From X-ray structure analysis, the $V^{IV}-O-V^{IV}$ angle was found to be $\sim 115^\circ$ and 180° in **1** and **2** respectively. Upon one-electron reduction selectively at one V centre at an appropriate potential, each of **1** and **2** generated mixed-valence $[(HL)V^{IV}O-(\mu-O)-OV^{IV}(HL)]^-$ species **1A** and **2A** respectively, which showed valence delocalization at room temperature and localization at 77 K, and the $V^{IV}-O-V^{IV}$ bond angles were calculated to be 177.5° and 180° respectively. The intercalative mode of binding of the two complexes **1** and **2** with CT DNA has been suggested by UV-visible spectroscopy ($K_b = 7.31 \times 10^5 \text{ M}^{-1}$ and $8.71 \times 10^5 \text{ M}^{-1}$ respectively for **1** and **2**), fluorescence spectroscopy ($K_{sv} = 6.85 \times 10^5 \text{ M}^{-1}$ and $8.53 \times 10^5 \text{ M}^{-1}$ respectively for **1** and **2**) and circular dichroism spectroscopy. Such intercalative mode of binding of these two complexes with CT DNA and HPV DNA has also been confirmed by molecular docking study. Both complexes **1** and **2** exhibited promising anti-cancer activity against SiHa cervical cancer cells with IC_{50} values of $28 \pm 0.5 \mu\text{M}$ and $25 \pm 0.5 \mu\text{M}$ respectively for 24 h which is significantly better than that of widely used cisplatin (with IC_{50} value of $63.5 \mu\text{M}$). Nuclear staining experiments reveal that these complexes kill the SiHa cells through apoptotic mode. It is interesting to note that these two complexes are non-toxic to normal T293 cell line. Complex **2** showed higher DNA binding ability with CT DNA and HPV DNA as well as better anti-cancer properties towards SiHa cervical cancer cells in comparison to complex **1**, a fact which can be explained by considering the lower energy of LUMO (which favours electron transition from DNA to the metal complex) and also the higher surface area of complex **2** in comparison to complex **1** due to the presence of one extra electron-withdrawing phenyl group in the former.

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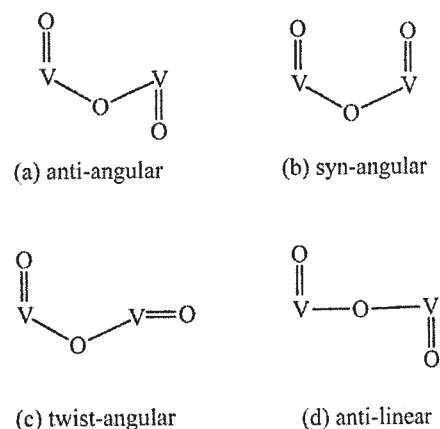
^aPost Graduate Department of Chemistry, Ramakrishna Mission Vivekananda Centenary College, Rahara, Kolkata-700118, India. E-mail: ictg_64@yahoo.co.in^bDepartment of Botany, University of Calcutta, 35 Ballygunge Circular Road, Kolkata-700019, India^cDepartment of Chemistry, Jadavpur University, Kolkata-700032, India^dDepartment of Chemistry, Ramakrishna Mission Residential College, Narendrapur, Kolkata-700103, India^eDepartment of Chemistry, The University of Reading, PO Box 224, Whiteknights, Reading, RG6, 6AD, UK†Electronic supplementary information (ESI) available: The structure of the ligands present in the complexes mentioned in Table 4 (Scheme S1); different type of interactions between CT DNA and HPV 18 DNA with the complexes obtained from molecular docking study (Table S1); cyclic voltammograms of complexes **1** and **2** (Fig. S1); X-band EPR spectra of complex **1A** in CH_2Cl_2 solu-tion at 300 K and at 77 K (Fig. S2); electronic spectra of **2A** in CH_2Cl_2 solution (Fig. S3); DFT optimized structures of **1** and **2** (Fig. S4); absorption spectra of complex **2** in the presence of increasing amounts of CT DNA (Fig. S5); fluorescence spectra of (1st) EB + 10^{-4} M DNA control and (2nd)–(11th) EB + DNA + $(1-10) \times 10^{-5}$ M of complex **2** (Fig. S6); circular dichroism spectra of 60 μM CT DNA in 10 mM Tris-HCl buffer (pH 7.2) titrated with 10–40 μM complex **2** (Fig. S7); MTT assay showing cell viability of SiHa cells treated with complexes **1** and **2** (concentration range: 40–240 μM), bars representing SD of three independent replicates (Fig. S8); study of apoptosis by morphological changes in nuclei of SiHa cells on applying complex **1** (Fig. S9); docked pose of complex **2** showing interaction with CT DNA base pairs (Fig. S10); docked pose of complex **2** showing interaction with HPV 18 DNA base pairs (Fig. S11). CCDC 1575573 and 1575574. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7dt03585c

1. Introduction

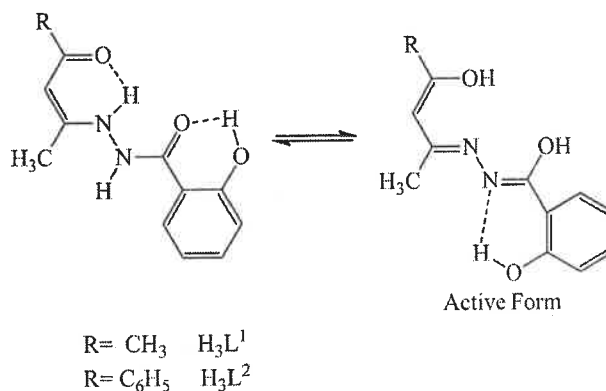
The significant abundance of vanadium (30 nM) in sea water,¹ the functionality (redox activity or Lewis acidity) relevant to biological processes of its commonly occurring stable oxidation states (*viz.*, III, IV and V) and negligible toxicity at physiological pH make it suitable for a bio-element. The biological function of vanadium is well established and has been well documented.^{2–4} Vanadium complexes have the ability to suppress the growth of existing tumours by inhibiting tumour cell proliferation, including apoptosis and limiting the invasion and metastatic potential of neoplastic cells.⁵ Presently, cervical cancer which originates mainly due to HPV oncogenic infection is of great concern.⁶ The prevalence of cervical cancer, associated with high-risk HPVs 9HPV (16/18), is greater in developing countries than developed countries.⁷ Cisplatin is widely used in various types of cancer chemotherapy including cervical cancer.⁸ However, it has several undesirable side effects⁹ (*viz.*, high nephrotoxicity, neurotoxicity, hair loss, vomiting tendency and drug resistance of metastatic cancer) and for this reason complexes using other transition metals (*e.g.*, Ru, Au, V and Cu) have been developed and approved for *in vivo* clinical trials in various types of cancer treatment.¹⁰ In this context, a suitably designed vanadium complex containing biologically relevant ligands having lesser side effects may be a promising candidate in cervical cancer chemotherapy.

From this perspective, a vanadium complex containing the $V_2O_3^{4+}$ motif (as in the stable +V state, vanadium can exist in three motifs, namely VO^{3+} , $V_2O_3^{4+}$ and VO_2^+) may be the most suitable candidate because in one molecule two V centres are present. On the other hand, from the inorganic chemists' point of view, complexes containing this motif are also important due to: (i) structural diversity with identical ligand molecules attached to both the metal centres,^{11–21} resulting from the different V–O–V bond angles, ranging from linear to angular, along with disposition of the terminal oxido atoms from anti-linear¹¹ⁱ to syn-angular^{11df,14b,17–21} through anti-angular^{11a–c,e,g,h} and twist-angular^{11g,h,12a,b,13a,b} structures (Scheme 1) and (ii) interesting magnetic behaviour of the mixed-valence $V_2O_3^{3+}$ species, generated from the $V_2O_3^{4+}$ analogue after electro-reduction of one vanadium centre selectively in order to disclose the locality of the electron and the state of metal oxidation.

Based on this background, we have utilized two hydrazone ligands (H_3L^1 and H_3L^2 , general abbreviation H_3L ; Scheme 2) which were derived from the condensation of 2-hydroxybenzoylhydrazide (hereafter H_2bh) with acetylacetone (H_3L^1) and benzoylacetone (H_3L^2), as hydrazone moieties are important pharmaceutical cores of several anti-cancer, anti-inflammatory and anti-platelet drugs.²² These two ligands have identical donor sites but a different substituent in the ligand structures, *i.e.*, one of the two CH_3 groups in the β -diketone part of H_3L^1 ligand is replaced by a C_6H_5 group in the H_3L^2 ligand. The replacement of an electron-donating CH_3 group by a more bulky and electron-withdrawing C_6H_5 group is expected to change the property of the ligand and hence of the complex contain-



Scheme 1 Possible configurations of the bridge and terminal oxygen atoms in $[V_2O_3]^{4+}$ core.



Scheme 2 Hydrazone ligands used in this study.

ing this ligand for the following reasons: (i) the electron-withdrawing C_6H_5 group can decrease the basic property of the ligand particularly of the donor moiety close to this group thereby increasing the electron acceptor property of the resulting complex, (ii) it can change the energies of the frontier orbitals of the resulting complexes and (iii) it can influence the bond angles of vanadium donor atoms in the complex through steric effects. In fact, this work was done to explore the effect of these substituents in the β -diketone part of the hydrazone ligands (i) on the V–O–V angle, if any, in the complexes with $V_2O_3^{4+}$ motif containing these hydrazone ligands, (ii) on the DNA binding ability of the resulting μ -oxidodivanadium(v) complexes and (iii) on the anticancer activity of these complexes against cervical cancer cells, if any. The locality of the odd electron in the mixed-valence $V^{IV}-O-V^V$ species electro-generated from the respective V^V-O-V^V analogue has also been studied.

The hydrazone ligands used in this study contain five donor sites with varying basicity, namely one enolic, one phenolic, one amide and two imine moieties, but in their complexes (1 and 2) they behave as tridentate dinegative ONO donors utilizing the enolic, amide and one imine moieties