

## A colorimetric sensor based on 3,5-dihydroxytoluene and 4-nitrophenyl for anion detection

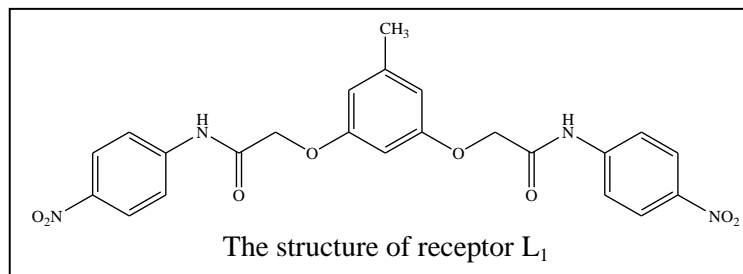
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2,2'-(5-Methyl-1,3-phenylene)bis(oxy)bis(N-(4-nitrophenyl)acetamide), L<sub>1</sub>, has been synthesized and explored its properties as a colorimetric sensor. Interactions of receptor L<sub>1</sub> with various anions are investigated by using <sup>1</sup>H NMR and UV-vis spectroscopy. From <sup>1</sup>H NMR studies in DMSO, the signal of NH protons of receptor L<sub>1</sub> was found at 10.65 ppm. These protons disappeared after addition of anions (fluoride, acetate, phosphate and benzoate) via deprotonation process. Moreover, the aromatic protons of receptor L<sub>1</sub> shifted upfield due to enhancement of negative charges in the system. From UV-vis titration in DMSO, the absorption at 328 nm of receptor L<sub>1</sub> gradually decreased upon the increment of anions. In the case of fluoride and acetate ions, a respective isosbestic point and new absorption band were observed at 386 nm and 447 nm for fluoride ion and at 400 nm and 443 nm for acetate ion. The color solution of receptor L<sub>1</sub> in DMSO changed from pale yellow to orange and dark yellow in the presence of fluoride and acetate ions, respectively. These results indicated that receptor L<sub>1</sub> underwent the charge transfer transition upon interaction with anions. The receptor L<sub>1</sub> is highly selective to fluoride ion over other anions. The ratio of 1:1 complex between receptor L<sub>1</sub> and fluoride ion was identified by Job's method.



**Keywords** colorimetric sensor; fluoride and acetate ion; 4-nitrophenyl

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## Synthesis and Characterization of Copper(II) and Nickel(II) Complexes of Hexazamacrocyclic Ligands

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Two new complexes, [CuL](ClO<sub>4</sub>)<sub>2</sub> (**1**) and [NiL](ClO<sub>4</sub>)<sub>2</sub> (**2**), of the hexazamacrocyclic ligand 3,10-dioctyl-1,3,5,8,10,12-hexaazacyclotetradecane (**L**), were synthesized by one-pot condensation of ethylenediamine, formaldehyde, and octylamine in the presence of copper(II) and nickel(II) salts, respectively. The complexes were characterized by elemental analyses (CHN/O), liquid chromatography-mass spectrometry (LC-MS), Fourier transformed infrared spectroscopy (FT-IR), and UV-Vis spectroscopy. Data from these techniques indicated that each metal ion combined with one ligand **L** with the presence of two perchlorate anions. The structures of these two complexes were then proposed to consist of metal-ion center, Ni(II) or Cu(II), coordinated by four secondary amine nitrogen donors of the hexazamacrocyclic ligand to form a square-planar geometry forming five- and six-membered macrocyclic rings.

**Keywords** Hexazamacrocyclic ligands; Spectroscopy technique; One-pot condensation; Macrocyclic copper(II) complexes; Macrocyclic nickel(II) complexes

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## Some first row transition complexes with acetylacetonate and tetraazamacrocyclic ligands for antibacterial activity

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The complexes with two types of ligands; metal acetylacetonate complexes ( $M(\text{acac})_2$  where  $M = \text{Cu(II)}$ , ( $\text{acac}$ ) = acetylacetonate and  $M(\text{acac})_3$  where  $M = \text{Al(III)}$ ,  $\text{Mn(III)}$ ,  $\text{Fe(III)}$  and  $\text{Co(III)}$ ) and metal tetraazamacrocyclic complexes ( $\text{ML}[1]$  and  $\text{ML}[2]$ , where  $M = \text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  and  $\text{L}[1] = 5,7,7,12,14,14\text{-hexamethyl-1,4,8,11-tetraazacyclotetradeca 4,11-diene perchlorate}$  and  $\text{L}[2] = 7,14\text{-diethyl-5,6,7,12,13,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca 4,11-diene perchlorate}$ ) have been synthesized and characterized by using elemental CHN analysis. The structures of synthesized complexes were confirmed by IR,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , UV-Vis spectroscopy. All the compounds have been screened for their antibacterial activity, using disc diffusion technique. The microorganism used for antibacterial investigation included *Escherichia coli* (*E. coli*) and *staphylococcus aureus* (*S. aureus*). The all complexes exhibited appreciable activity, especially  $\text{CuL}[1]$  and  $\text{NiL}[1]$ , suggesting highly potential to develop for medical applications.

**Keywords** First row transition; Acetylacetonate ligand; Tetraazamacrocyclic ligand; Antibacterial activity

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# Synthesis of Magnetic Nanoparticles Coated with Biocompatible Polymers for Drug Delivery Application

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Magnetic nanoparticles (MNPs) have received much attention in medicinal applications especially in protein delivery systems. The MNP protein delivery has advantages because they can carry protein and be directed to target cells using an external magnetic field. In this study, we are interested in the synthesis of MNPs with coating polymers. The MNPs were first synthesized by thermal decomposition method and co-precipitation method. Then, MNPs were coated with two biocompatible polymers; poly (lactic-co-glycolic acid), PLGA and modified polyacrylic acid (mPAA). The effect of magnetic to polymer ratio on the nanoparticles size have been investigated. The particle size, shape of nanoparticles and polymer were characterized by various techniques including transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), dynamic light scattering (DLS) and infrared spectroscopy (IR). The results showed that MNPs from thermal decomposition method with about 15 nm in diameter were obtained, while MNPs after coated with polymers have diameter of around 100 nm. For future vaccine delivery, cytotoxic effects of these nanoparticles and solvents were tested using MTT assay.

**Keywords** Magnetic nanoparticles; Drug delivery; Biocompatible polymer

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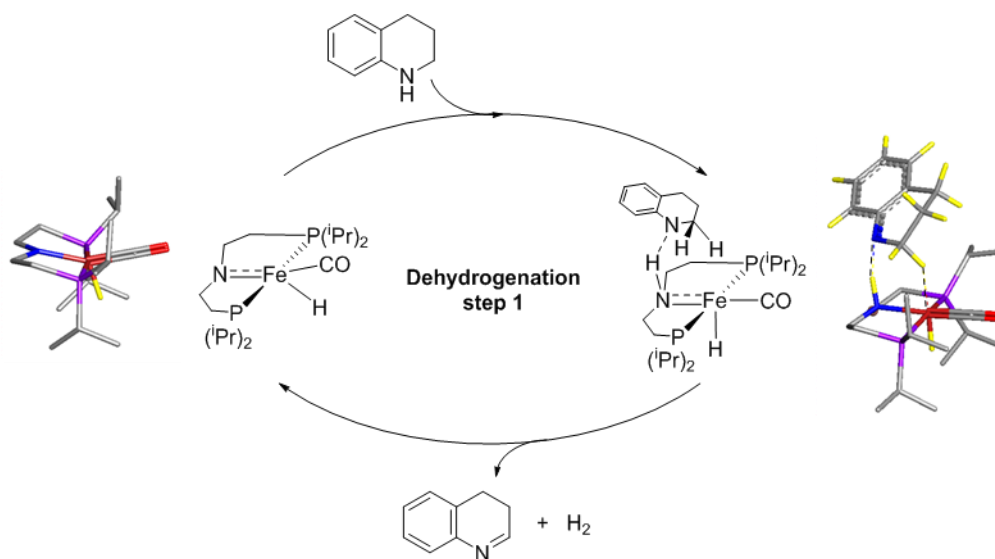
# Mechanistic Study of Dehydrogenation and Hydrogenation of N-Heterocycles using Pincer-Supported Iron-Catalyst

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Dehydrogenation and hydrogenation of N-heterocyclic compounds are useful for pharmaceutical and organic synthesis. As two hydrogen molecules can be released and captured per one N-heterocyclic molecule, these processes can be applied for organic hydrogen storage. The catalysts that can activate both reactions are normally iridium(III) complexes with pentamethylcyclopentadienyl ligand (Cp\*). Recently, Jones and coworkers revealed that iron(II) complex with bis(phosphino)amine (PNP) pincer ligands,  $\text{Fe}^{(\text{iPr})\text{PNP}}(\text{CO})(\text{H})$ , can catalyze both dehydrogenation and hydrogenation of N-heterocycles in good yields [1]. However, the reaction mechanisms are still not clear. Here, we performed density functional calculations to study the mechanism of dehydrogenation of 1,2,3,4-Tetrahydroquinoline (THQ) catalyzed by  $\text{Fe}^{(\text{iPr})\text{PNP}}(\text{CO})(\text{H})$ . We found that THQ first binds to  $\text{Fe}^{(\text{iPr})\text{PNP}}(\text{CO})(\text{H})$  with a weak hydrogen-bonding interaction between proton of amine on THQ and N atom of PNP ligand, followed by the H-transfer from the adjacent  $\text{CH}_2$  on THQ to the Fe. N-atom of 1,2,3,4-Tetrahydroquinoline is important for the binding of the substrate to the Fe catalyst, which facilitates the dehydrogenation process. Without the amine group in the substrate, the reaction cannot occur due to the lack of hydrogen bonding.



**Keywords** DFT; Dehydrogenation; Hydrogenation; Iron-catalyst; N-heterocycles

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## One Pot Synthesis of Free Base *meso*-Tetra (Substituted Phenyl) Porphyrins

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In this work, a series of *meso*-tetra (substituted phenyl) porphyrins was synthesized and characterized. A modified Adler method was used for the synthesis of symmetrical porphyrins by condensation reaction between pyrrole and different substituted benzaldehydes in propionic acid. The synthesized porphyrins were characterized by using proton nuclear magnetic resonance spectroscopy, ultraviolet–visible spectroscopy, fluorescence spectroscopy, mass spectrometry and thermogravimetric analysis. This research was studied the trend of free base porphyrins when the aldehyde precursors were different in the ability to provide electron density to the  $\pi$  system. The aldehyde precursors were included benzaldehyde, 4-hydroxybenzaldehyde, 4-methoxybenzaldehyde and 4-carboxybenzaldehyde. The product yield of TPP, THPP, TMPP, TCPP are 36.0%, 25.7%, 6.2% and 36.2%, respectively. The spectroscopic information of synthesized compounds is confirming the expected structure. The results show that one pot synthesis reaction is successful.

**Keyword** Free base porphyrins; Symmetrical porphyrins; Adler method

# Synthesis and Characterization of Long Chained Porphyrin Derivatives and Cobalt Complexes

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In the present work, the synthesis and properties of long chained porphyrin and their cobalt complexes were examined. The compounds were synthesized by Adler-Longo method, refluxing aldehyde and pyrrole in propionic acid. The long chained on *para*-position of porphyrins are including tetrakis (4-methoxyphenyl) porphyrin (TOMPP), *tetrakis* (4-butyloxyphenyl) porphyrin (TOBPP), *tetrakis* (4-octyloxyphenyl) porphyrin (TOOPP) and *tetrakis* (4-decyloxyphenyl) porphyrin (TODPP). The products were obtained in 26%, 5%, 13 and 14% yields, respectively. Further refluxing the respective ligands with cobalt acetate in DMF gave CoTOMPP, CoTOBPP, CoTOOPP and CoTODPP, respectively with yields ranging from 75 to 92% yields. All ligands and complexes are characterized by <sup>1</sup>H-NMR, MS, IR, UV-Vis and fluorescence spectroscopy, and the results are in agreement with the expected structures.

**Keywords** Porphyrin; Long chain; Cobalt porphyrins; Spectroscopy

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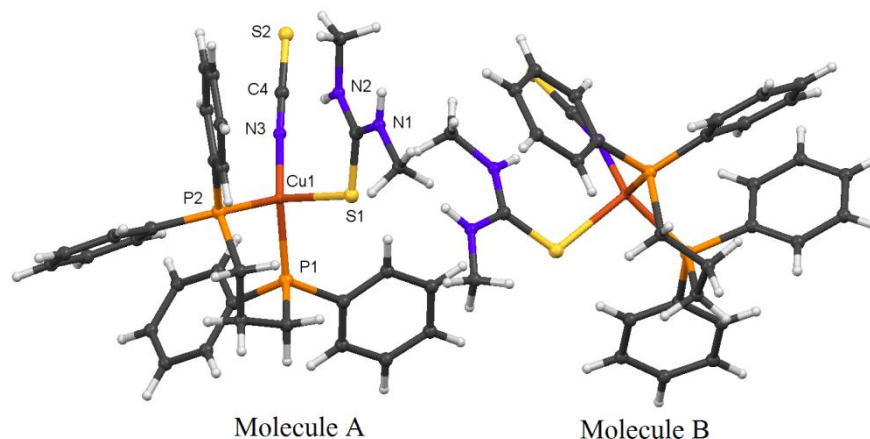
## Synthesis, X-Ray Studies of Mixed Ligand Complex of Copper(I) Thiocyanate with *N,N'*-Dimethylthiourea and Bis(diphenylphosphino)propane

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Reaction of copper(I) thiocyanate with *N,N'*-dimethylthiourea (dmu) and Bis (diphenylphosphino) propane (dppp) in acetonitrile (1:1:1 molar ratio) has yielded mononuclear complex of general formula, [Cu(NCS)(dppp)(dmu)]. The complex crystallizes in monoclinic system, space group  $P2_1$  (No.4). Cu<sup>I</sup> centre ion exhibit a pseudo distorted tetrahedral geometry, with coordination sphere of Cu<sup>I</sup> centre ion of two P atoms from one dppp molecule, one terminal exocyclic S-thiourea of one terminal dmu molecule and one terminal N atom of terminal thiocyanate. The complex consists of two independent [CuSCN(dppp)(dmu)] molecules with above stoichiometry in asymmetric unit. The dppp ligand is involved in the bidentate coordination mode with copper atoms, forming a six-member ring CuP<sub>2</sub>C<sub>3</sub>. The coordination of the dmu ligand is further stabilized by intra-molecular N—H···N hydrogen bond with N···N distance of 3.265 (4) Å. The intramolecular hydrogen bonds in both molecules correspond with S(6) for the six atoms comprising the intramolecular pattern. In the crystal, molecules are linked by N—H···S hydrogen bonds forming a zigzag chain along the *a*-axis direction.



**Figure 1** The molecular structure with displacement ellipsoids drawn at the 50% probability level

**Keywords** Diphosphine; Dimethylthiourea; Copper(I) complex; X-ray crystal structure



## Syntheses of Magnetic Nanocomposite Size Series

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Different sizes of composites of magnetic nanoparticles (MNPs) with narrow size distribution were synthesized by two pathways. In the first method, the magnetite ( $\text{Fe}_3\text{O}_4$ ) MNPs were prepared via thermal decomposition of iron oleate complex at above  $290^\circ\text{C}$ . The resulted  $\text{Fe}_3\text{O}_4$  NPs were then coated by silica using reverse microemulsion method, and the core-shell nanostructures of  $\text{Fe}_3\text{O}_4$  MNP@ $\text{SiO}_2$  were obtained. For the other pathway, core-shell MNP@ $\text{SiO}_2$  synthesized according to the first pathway were further functionalized with 3-aminopropyltrimethoxysilane to afford  $\text{NH}_2$ -functionalized MNPs ( $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$ - $\text{NH}_2$ ). Then, we prepare silica nanoparticles ( $\text{SiO}_2$  NPs) with the diameter of 50-100 nm using reverse microemulsion method. In the final step,  $\text{Fe}_3\text{O}_4$ @ $\text{SiO}_2$ - $\text{NH}_2$  and  $\text{SiO}_2$  NPs were combined using electrostatic attraction to produce  $\text{SiO}_2$ - $\text{Fe}_3\text{O}_4$  nanocomposites. With these two synthetic pathways, the controlled sizes of the MNP composites ranging from 20 to 150 nm in diameter with narrow size distribution were obtained. These size series of magnetic nanocomposites are useful tools to understand the effect of sizes, surfaces, and magnetization in various applications including magnetic separation and magnetically-guided drug delivery.

**Keywords** Magnetic nanoparticles (MNPs); Thermal decomposition technique; Magnetic nanocomposites

# Preparation of Perchlorate Anion Selective Membrane Electrodes from Donnan Exclusion Failure Phenomenon Induced by Metal Ions

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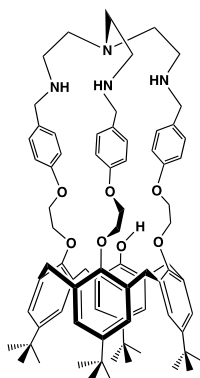
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A calix[4]arene derivative, tripodal amine crown ether calix[4]arene, L1 was synthesized and used as ionophore or ion carrier which incorporated in the *o*-nitrophenyl octyl ether (*o*-NPOE) plasticized PVC membrane ion selective electrodes (ISE). The prepared ion selective membrane also contained potassium tetrakis(*p*-chlorophenyl)borate (KTPCIPB) as anionic additive. The membrane containing L1 showed Donnan exclusion failure because the ionophore bound tightly to metal ions such as Cu<sup>2+</sup> and Zn<sup>2+</sup> ions. The influence of positive charges of metals could induce the co-extraction of anions into the membranes that changed the permselectivity of the membrane to the negative direction. The fabricated electrodes containing L1 with KTPCIPB as anionic additive preconditioning in CuCl<sub>2</sub> and ZnCl<sub>2</sub> illustrated the highest selective toward perchlorate with slopes of -56.11 and -56.58 mV decade<sup>-1</sup>, respectively over a wide concentration range of ClO<sub>4</sub><sup>-</sup> (10<sup>-5</sup> to 10<sup>-2</sup> M) with detection limits as low as 2.88 x 10<sup>-6</sup> and 2.78 x 10<sup>-6</sup> M, respectively. In addition, the fabricated membrane electrodes could be used in a wide pH range with good ISE characteristics.



Tripodal amine crown ether calix[4]arene (L1)

**Keywords** Donnan exclusion failure; Perchlorate selective electrode; Calix[4]arene

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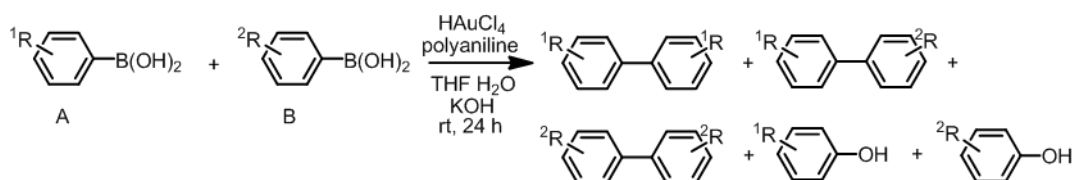
## Gold Nanoparticles with Polyaniline for Selective Coupling and Oxidation Reactions of Aryl Boronic and Its Substitutes

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Gold catalysts were investigated for the selective transformation of aryl boronic acids in different pathways: (I) Coupling reaction and (II) Oxidation reaction. Polyaniline and its derivatives for example poly-(m-aminophenol), poly-(m-aminoaniline), poly-(m-aminothiobenzene) and poly-(m-aminonitrobenzene) were considered as stabilizing ligands of gold nanocatalysts to transform the reaction selectively. In (I) coupling reaction, aryl boronic A and B were used as starting materials to study the effect of selective coupling products, homocoupling and cross coupling, resulted from different polyanilines. For (II) oxidation reaction, phenol products were considered as byproducts of the coupling reaction. This research suggested how to tune the catalytic activity of gold nanocatalysts selectively by variation of polyanilines.



**Keywords** Gold; Nanocatalyst; Polyaniline; Coupling; Oxidation

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## Synthesis and Crystal Structure of Silver(I) Chloride Complex with *N*-allylthiourea and Triphenylphosphine

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The complex of  $[\text{Ag}(\text{Altu})(\text{PPh}_3)_2\text{Cl}]\cdot\text{CH}_3\text{CN}$  was synthesized by the reaction of silver(I) chloride with *N*-allylthiourea (Altu) and triphenylphosphine (PPh<sub>3</sub>). The structure has been characterized by single crystal X-ray diffraction, Fourier transform infrared spectroscopy and nuclear magnetic resonance spectroscopy. The complex crystallizes in *P* $\bar{1}$  with cell parameters  $a = 11.0537(4) \text{ \AA}$ ,  $b = 13.1661(5) \text{ \AA}$ ,  $c = 14.6392(5) \text{ \AA}$ ,  $\alpha = 99.2140(10)^\circ$ ,  $\beta = 99.1030(10)^\circ$ ,  $\gamma = 92.5920(10)^\circ$ ,  $V = 2071.08(13) \text{ \AA}^3$  and  $Z = 2$ . The Ag(I) ion is four-coordinated by one Altu molecule, two PPh<sub>3</sub> molecules and one chloride ion, forming a distorted tetrahedral geometry.

**Keywords** Crystal structure; Silver(I) complex; *N*-allylthiourea

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## Synthesis and Characterization of Cadmium(II) Complex with 4,4'-Bipyridine and Cinnamic Acid

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[Cd<sub>3</sub>(4,4'-bipyridine)<sub>2</sub>(cinnamate)<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> was synthesized using hydrothermal method with Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, 4,4'-bipyridine, and cinnamic acid as starting materials. The obtained complex was investigated by Fourier transformed infrared spectroscopy (FT-IR), single crystal x-ray diffraction (SCXRD), and thermogravimetric analysis (TGA). Single crystal x-ray diffraction study revealed that the complex crystallized in triclinic space group  $P\bar{1}$ . The octahedral geometry Cd(1) was coordinated by four oxygen atoms from cinnamate ligand and two oxygen atoms from water molecules, while Cd(2) and Cd(3) were coordinated by five oxygen atoms from cinnamate ligand in the equatorial position and the axial position by two nitrogen atoms from 4,4'-bipyridine ligand, forming a pentagonal bipyramidal geometry.

**Keywords** Supramolecular; 4,4'-Bipyridine ligand; Hydrothermal condition; Thermal analysis

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## **Synthesis of calcium silicate from shell of *Pomacea canaliculata* and rice husk ash by mechanochemical method**

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Calcium silicate was synthesized using silica from rice husk ash and calcium oxide from shell of snail namely *Pomacea canaliculata* calcined at 800 °C for 2 hours. The rice husk ash and calcined shell in molar ratio of 1:1 were ground by alumina ball with high speed milling. The solid powder was calcined at 800 and 1000 °C for 2 hours. The formation of calcium silicate was firstly investigated by Fourier transform infrared spectroscopy. The temperature for calcination could affect the occurring of calcium silicate with appearance the band of Ca–O–Si at 935 cm<sup>-1</sup>. Calcium silicate was starting occurred while mixed oxide was ground for 1 hour and calcined at 1000 °C. The phase of calcium silicate was confirmed by X-ray diffractometry.

**Keywords** Calcium silicate; Shell of *Pomacea canaliculata*; Rice husk ash; Mechanochemical method

## Equilibrium Extraction of Uranium and Thorium Mixtures in 4 M HNO<sub>3</sub> with 5 and 10% TBP/Kerosene

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Solvent extraction technique has been used extensively for the separation and purification of uranium and thorium from other associated elements in the nuclear materials processing. In this work, the equilibrium extraction of uranium and thorium from 4 M HNO<sub>3</sub> with 5 and 10% tributyl phosphate (TBP) in kerosene was investigated. The distribution coefficients of each element were studied at various concentrations of the individual solution and of the mixed solution. The element concentration was determined by ICP-AES. The distribution coefficients of both uranium and thorium were found to be varied with their concentration and the distribution coefficient of uranium is much higher than that of thorium. The extraction efficiency increased with higher TBP concentration but decreased with the increasing feed concentration. The uranium-thorium separation factor in the mixed solution was seen to depend on the mixture concentration and 10% TBP/kerosene extractant provided higher uranium-thorium separation factor than 5% TBP/kerosene. These equilibrium data are further developed according to the McCabe-Thiele approach to simulate the multistage counter-current extraction and separation of uranium and thorium mixtures.

**Keywords** Uranium; Thorium; Equilibrium; TBP; Solvent extraction

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## Reusable Photocatalytically Active Anatase Chitosan film.

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Anatase titania chitosan (A-CS) films were prepared with different ratios of chitosan and TiO<sub>2</sub> (CS:TiO<sub>2</sub> = 1:2 and 1:3). The characteristic of A-CS films were determined by XRD, FTIR and SEM. The photocatalytic activity of A-CS films were investigated by monitoring the decolorization of methylene blue, which represents dye model pollutant, under UV light. In photocatalytic experiment, the A-CS films can be easily recovered from solution compared to TiO<sub>2</sub> powder. Furthermore, the reusable A-CS films in degradation of methylene blue were also studied. The result showed that the A-CS film was a good candidate for recyclable dye remover in water treatment because of its good performance in photocatalytic activity, reusable and compatible material for green chemistry.

**Keywords** Anatase; TiO<sub>2</sub>; Chitosan film; Photocatalytic activity



## Responsive Probes Based on Luminescent Iridium Complexes

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A series of luminescent iridium complexes has been synthesized. All of the synthesized complexes contain two cyclometalating phenylpyridine (ppy) ligands. The third ligand bound to iridium is either a diimine (e.g. 2,2'-bipyridine) or another ppy based ligand. The identity of the third ligand thus splits the synthesized complexes into two distinct groups; positively (+1) charged heteroleptic iridium complexes and neutral triscyclometalated iridium complexes. The positively charged complexes have been isolated as their hexafluorophosphate (PF<sub>6</sub><sup>-</sup>) salts. These iridium complexes were synthesized with the aim of developing responsive luminescent probes. Complexes synthesized so far show response to Fe<sup>3+</sup> ions, water/moisture, and hydride reducing agents. Characterization of the synthesized complexes has been carried out using <sup>1</sup>H NMR and MS. The photophysical properties and responsive characteristics are being investigated using UV-Vis and fluorescence spectroscopies.

**Keywords** Luminescent; Iridium complexes; Responsive probes

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# Self-Assembly of Novel Silver(I) Coordination Polymers with 1,4-Phenylenedimethylylidene-bis-4-haloaniline Ligands: Crystal Structures and Luminescence Properties

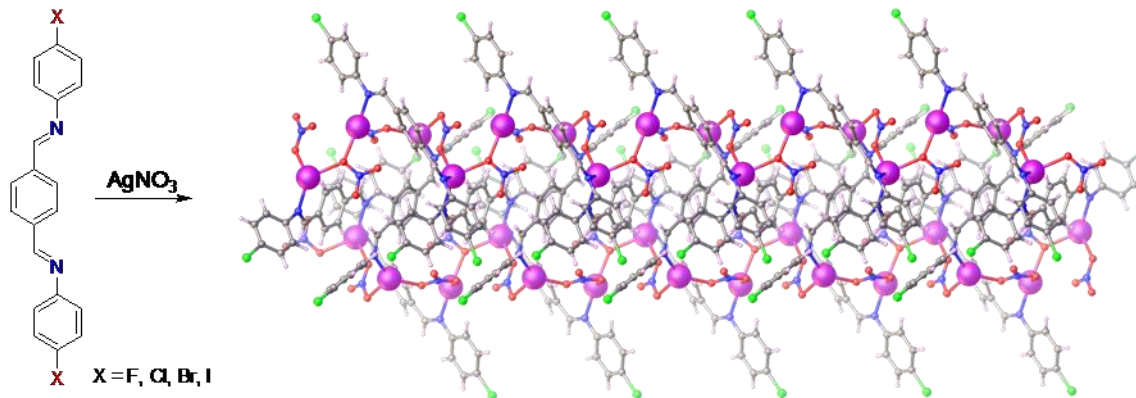
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New flexible *N*-donor ligands of 1,4-phenylenedimethylylidene-bis-4-haloaniline (PB-XA) were designed and successfully synthesized by the coupling reaction between benzene-1,4-dicarbaldehyde and corresponding 4-haloaniline in a 1:2 ratio using THF at 110 °C for 6 h. Self-assembly reactions of these ligands with silver(I) nitrate in a mixture solution of MeOH and CH<sub>2</sub>Cl<sub>2</sub> gave a new series of silver(I) coordination polymers with the general formula [Ag<sub>3</sub>(PB-XA)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>], where X = F (1), Cl (2), Br (3), I (4). All compounds are isostructural and can be crystallized in the centrosymmetric triclinic space group *P*-1 with three independent Ag(I) atoms in the asymmetric unit. The Ag(I) ions are linked by the PB-XA and NO<sub>3</sub> molecules to form a one-dimensional chain along the crystallographic *b* axis with the Ag⋯Ag separations lie in the range 4.2 - 5.3 Å. These chains are further linked into a three-dimensional network *via* π⋯π stacking and weak C-H⋯X halogen bonds. The luminescence properties of these compounds were also investigated in the solid state at room temperature and 77 K.



**Keywords** Coordination polymers; Crystallography; Ligands; Photoluminescence; Silver(I)

## Temperature-Dependent Structures and Gas Adsorption Behaviors in Porous Lanthanide Coordination Polymers

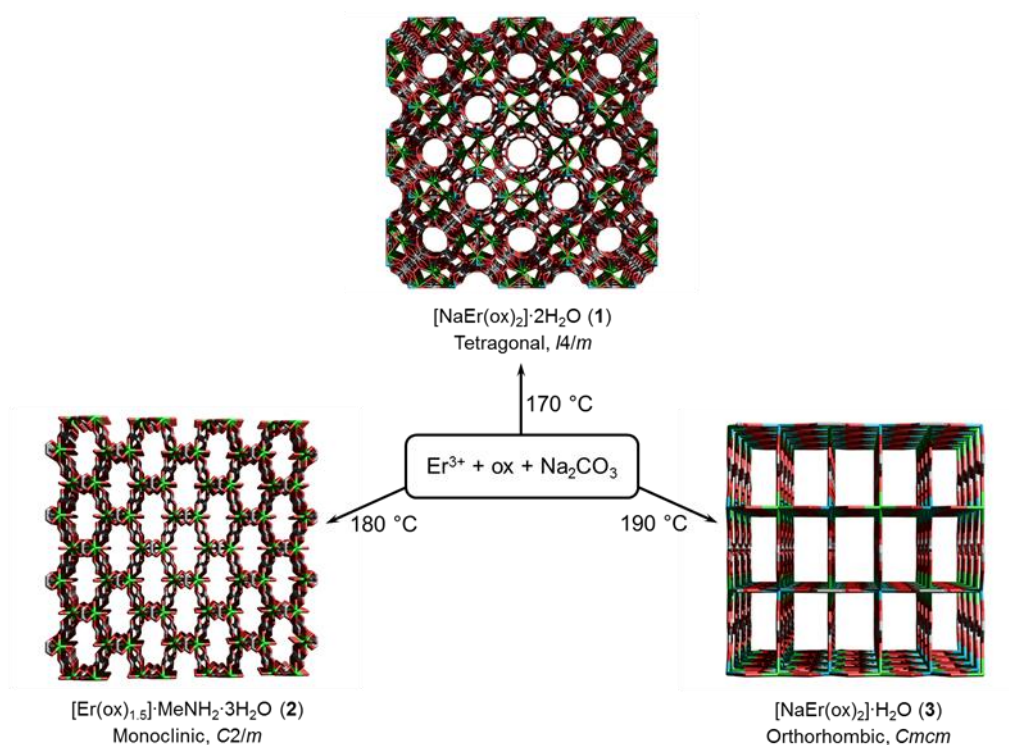
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Three new three-dimensional (3D) porous lanthanide coordination polymers,  $[\text{NaEr}(\text{ox})_2] \cdot 2\text{H}_2\text{O}$  (**1**),  $[\text{Er}(\text{ox})_2(\text{H}_2\text{O})] \cdot (\text{MeNH}_2) \cdot 3\text{H}_2\text{O}$  (**2**) and  $[\text{NaEr}(\text{ox})_2] \cdot \text{H}_2\text{O}$  (**3**), have been synthesized solvothermally from the self-assembly of erbium(III) ions and oxalic acid in the presence of sodium bicarbonate at the reaction temperature of 170, 180 and 190 °C, respectively. Compound **1** crystallizes in the tetragonal space group  $I4/m$  ( $Z = 16$ ) and possesses a 3D open-framework, **2** exhibits a 3D diamond framework with the monoclinic space group  $C2/m$  ( $Z = 8$ ), whereas **3** crystallizes in the orthorhombic space group  $Cmcm$  ( $Z = 4$ ) and also display a 3D open-framework. This study demonstrated that the reaction temperature plays an important role in the formation of different structures among compounds **1-3**. Gas adsorption studies were performed on these frameworks.



**Keywords** Coordination polymers; Erbium; Gas adsorption; Lanthanide; Oxalate

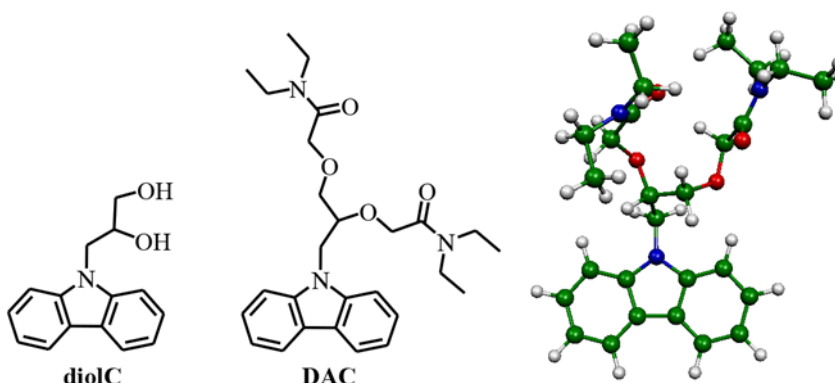
# The design, synthesis and complexation studies of the metal ions chemosensor based on carbazole derivatives: experimental and theoretical study

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Two Carbazole derivatives containing dihydroxyl (**DialC**) and *N,N*-dimethylacetamide (**DAC**) have been designed and synthesized for metal ions chemosensors. After characterization, the binding abilities between these chemosensors and various cations ( $K^+$ ,  $Ag^+$ ,  $Na^+$ ,  $Li^+$ ,  $Hg^{2+}$ ,  $Cd^{2+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Ba^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Pb^{2+}$ ,  $Fe^{2+}$ ,  $Zn^{2+}$ ,  $Cr^{3+}$ ,  $As^{3+}$ ,  $Al^{3+}$ ,  $Fe^{3+}$  or  $Ge^{4+}$ ) were studied using UV-Vis and fluorescent spectroscopic methods. Of all metal ions tested,  $Zn^{2+}$  showed dramatic change in both intensity and maximum wavelength in the spectra of the **DAC** chemosensors. The complexation behaviours were studied by UV-Vis titration. The binding properties of carbazole chemosensors with cations were also investigated using the density functional theory calculations at B3LYP/LanL2DZ level of theory. The calculated results point to the same conclusion. The DFT calculation also provided the HOMO-LUMO energy level, which explained the spectrum change upon complexation.



**Keywords** Carbazole; Fluorescence; Cation; Sensor; DFT

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## Development of Improved Iron Chelators

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A novel aroyl hydrazine compound *N*-(2-hydroxybenzyl)isonicotinohydrazide (BIH) derived from salicyl aldehyde has been synthesized as a potential iron chelator. BIH is a hydrazine analogue of the hydrazone iron chelator salicyl aldehyde isonicotinoyl hydrazide (SIH). BIH was designed to address the hydrolytic instability of SIH by reducing its hydrazone functionality into a hydrazine. BIH was prepared by a reaction of SIH with sodium borohydride in methanol and characterized using <sup>1</sup>H NMR and MS spectroscopies. The iron binding of BIH was investigated and compared to that of SIH using direct UV-Vis titration and a competition study with the fluorescent metal chelator calcein. Iron, the most abundant transition metal in human body, can take part in generating reactive oxygen species (ROS) through the Fenton reaction. Iron chelators can therefore act as protecting agents against the effects of oxidative stress. The ability of BIH to protect against oxidative stress was evaluated using deoxyribose assay and compared to SIH.

**Keywords** Iron; Chelators; Oxidative stress

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## Synthesis and Characterization of Tungsten Oxide/Titanium Oxide Composite.

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This current work has attempted to synthesize a composite of tungsten oxide ( $\text{WO}_3$ ) and titanium oxide ( $\text{TiO}_2$ ) via simple sol-gel and precipitation methods. Several previous methods prepared  $\text{WO}_3$  by precipitating tungstate salts in highly acidic solutions, followed by calcination; however, the syntheses in the similar conditions yielded  $\text{TiO}_2$  with poor crystallinity. In this study, the  $\text{WO}_3$ - $\text{TiO}_2$  composites were synthesized in acidic solutions through the precipitation of sodium tungstate ( $\text{Na}_2\text{WO}_4$ ) as a tungsten source combining with the hydrolysis and condensation of titanium isopropoxide ( $\text{Ti}(\text{O}^i\text{Pr})_4$ ) as a titanium source. The quantities of acid and water, as well as the adding orders of the reagents were varied. The obtained products were calcined at 500 and 700°C in air for 5 and 10 hours. From the X-ray powder diffraction (XRD) patterns, the crystal structures and crystallinities of the obtained products were strongly depended on the preparation condition, especially in highly acidic solution where the products were almost in amorphous phase.

**Keywords**  $\text{WO}_3$ ;  $\text{TiO}_2$ ; Composite; Sol-gel; XRD.

## Microwave assisted synthesis of MCM-41 and template removal by ion-exchange extraction under sonication

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Conventional hydrothermal synthesis of MCM-41 is slow and energy consuming. Moreover, the final calcination step wastes cetyltrimethylammonium bromide (CTAB) template and produces carbon dioxide. This work reports a fast synthesis of MCM-41 via microwave synthesis and the template recovery by ion-exchange extraction under sonication. For the synthesis, CTAB to silica molar ratio, crystallization time, and silica to sodium hydroxide molar ratio were optimized to improve the quality of MCM-41. The best gel composition in mole ratio was 3.34SiO<sub>2</sub>: 4.46 NaOH: CTAB: 1.16 H<sub>2</sub>SO<sub>4</sub>: 225H<sub>2</sub>O, based on the characteristic peak of (100), (110), (200) and (210) planes by x-ray powder diffraction technique. The quality of MCM-41 was improved with crystallization time in the range of 15–180 min. As for the template recovery, the effects from type of salt ions, solvents, extraction times, and temperatures were studied. Extraction in the presence of various ammonium salts retained the MCM-41 mesoporous structure. 70 % of CTAB removal was obtained with NH<sub>4</sub>Cl in methanol and the percent recovery increased with higher extraction times in the range of 15–120 min and extraction temperatures in the range of 30–60 °C.

**Keywords** MCM-41; Microwave; Ion-exchange extraction; Sonication

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## Synthesis of High Stability Zero-valent Fe Nanoparticles using Guava Leaf Extract as Green Stabilizer

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Plant extracts that contains polyphenolic compound can act as reducing agents and stabilizing agents in the green synthesis of novel nanoparticles. This work, polyphenolic compound were stabilizing agent because previous research had discover polyphenolic compound can't reduce Fe (III) ion but it can reduce Ag (III) ion and Au (III) ion were easy. High dispersion stability and mobility of zero-valent Fe nanoparticles ( $\text{Fe}^0$  nanoparticles) were successfully prepared by using guava leaf extract as a stabilizer. An aqueous guava leaves extract and aqueous solution of Fe (III) ion were mixed and adjusted the pH to 8. The strongly coloured Fe(III)-tannin complexes were formed. The results from NMR Spectroscopy showed that the structure of tannin. An aqueous solution of sodium borohydride was added to the complexes at room temperature as a reducing agent. Tannin-stabilized  $\text{Fe}^0$  nanoparticles were obtained. The results from TEM clearly showed that the synthesized tannin-stabilized  $\text{Fe}^0$  nanoparticles are roughly spherical and appear as discrete particles with the mean particle size around 10 nm. The results from the preliminary studies of stability and mobility showed that tannin-stabilized  $\text{Fe}^0$  nanoparticles remain suspended in water for more than a month and are able to pass through the column of sand. In addition, zeta potential analysis clearly confirmed their stability.

**Keywords** Zero-valent iron nanoparticles; Guava leaf extract; Green stabilizer

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# One-pot Synthesis of CuO/ZnO Nanostructure with Discrete CuO Nanoparticles on Tunable Size and Thickness of ZnO Nanoplate

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CuO/ZnO has been highlighted as a potential materials for sustainable conversion of carbon dioxide to methanol. This work, a new surface modified CuO/ZnO nanostructure was successfully synthesized by one-pot hydrothermal method. Heating an aqueous solution of zinc acetate and copper nitrate in the presence of hexamethylenetetramine (HMT) at 97°C and calcination at 500°C, discrete CuO nanoparticles surface segregated from ZnO nanoplate were obtained. The particle size and thickness of ZnO nanoplate can be tuned by varying mole percent of Cu<sup>2+</sup> adding. The Particle sizes, shape and morphology of the obtained products were investigated by Transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Crystal structure was identified by X-Ray diffraction (XRD). Chemical composition was confirmed by EDX analysis. Surface composition and oxidation state were study by X-Ray photoelectron spectroscopy (XPS). UV-Vis absorption spectroscopy and photoluminescence were used to further study of their optical properties.

**Keywords** Cu/ZnO nanoplate; One-pot synthesis

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## Effects of First Row Transition Metal Ions (Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup>) on the Porphyrin Derivatives

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The porphyrins and metalloporphyrins are heterocyclic macromolecules, in which transition metal ions are found in the central hole of porphyrins. In this study the free base porphyrins were prepared by a condensation reaction between pyrrole and various aldehydes in propionic acid following Adler-Longo method. The porphyrins were then refluxed with metals ions in the dimethylformamide (DMF) solvent before purification. The structures of porphyrins and porphyrin complexes were investigated by elemental analysis, mass spectrometry, infrared spectroscopy and NMR spectrometry. In addition, porphyrins and porphyrin complexes were also characterized by UV-Vis and fluorescence spectroscopy, in which the absorption spectra for free base porphyrins exhibit an extremely intense band (412-417 nm, Soret band). At longer wavelengths, the spectra contain a weaker set of 4 absorption bands (512-654 nm, Q-bands). Once the porphyrin macrocycles were coordinated to any metals, there was more symmetrical than in the free base porphyrins. Further they produced a simplification of Q bands pattern, with the formation of one to three Q bands, whereas their emission spectra of free base porphyrins show only a single peak in a range of 647-654 nm. Once, the metal ion was added into a free base porphyrin, it was found that the fluorescence intensity was increased. Their thermal behaviors, including a possible phase transition of porphyrins were studied during the heating process around 300-950 K. It was found that tetraphenyl porphyrin (TPP) ligand exhibits the lowest thermal stability in free base ligands, while Cobalt-methyltetraphenyl porphyrin complex (CoTMPP) possesses the greatest thermal stability (733.4 K) among synthesized porphyrins. The porphyrins and metalloporphyrin can be further modified to use as dye in the dye-sensitizer solar cells.

**Keyword** Porphyrin; Metalloporphyrin; TGA; NMR; Mass spectrometry

## Optical Sensing Properties of Plasticized Polymeric Membrane Incorporating N,N'-Ethylenebis(salicylimine) as Transition Metal Ion-Selective Ionophore

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Novel polymeric membrane optical sensors for the highly selective detection of transition metal ions using N,N'-Ethylene bis(salicylimine) (salen) as ionophore have been developed. The salen ligand was incorporated into plasticized PVC polymer matrix along with the presence of cation exchanger which has been varied in order to find the best performance sensor. Optical sensing properties of prepared sensors were then comparatively examined towards cations such as Al<sup>3+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> in terms of membrane sensitivity and selectivity, response time, linear concentration range, detection limit, working pH range, and also lifetime of sensor using UV-Vis spectrophotometric technique. The proposed membranes were found to be selective to Fe<sup>2+</sup> over other cations. The best performance optical sensor will be chosen and expected to be reusably applied for the determination of Fe<sup>2+</sup> in real water samples.

**Keywords** Optical sensor; Ionophore; N,N'-Ethylenebis(salicylimine)

## Novel Two-dimensional Square-grid Coordination Network of Zinc(II)-Pyridine-2,6-Dicarboxylate: *poly-bis*( $\mu_3$ -pyridine-2,6-dicarboxylato- $\kappa^5 N, O, O'$ )dizinc(II)

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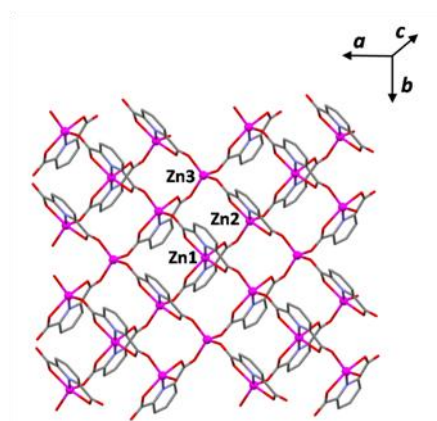
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The X-ray structure of title compound,  $\{Zn_2(C_7H_3NO_4)_2\}_n$  (**I**) comprised of three crystallographic independent Zn(II) centers which are connected together by pentadentate pyridine-2,6-dicarboxylato (dipic) ligands in *syn-anti* bridging mode. The coordination environments of these Zn(II) centers show different types of Zn-chromophore, namely  $[ZnN_2O_4]$  octahedral,  $[ZnNO_4]$  trigonal bipyramidal and  $[ZnO_4]$  tetrahedral geometries. The arrangement of dipic bridges to zinc centers plays an important role for generating an infinite two-dimensional square grid-type with (4,4) topology coordination network. This is a new example found for Zn-MOF containing only dipic ligand with three different Zn centers. These 2D layers are assembled via hydrogen bonding interactions, resulting to a 3D supramolecular framework.



**Keywords** Zinc(II); Pyridine-2,6-dicarboxylate; Two-dimensional network

## Improvement of catalytic performance of phenol hydroxylation by iron supported on ZSM-5

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The goal of this work was to improve catalytic performance for phenol hydroxylation on iron supported on ZSM-5. The ZSM-5 zeolite in sodium form (NaZSM-5) was synthesized by hydrothermal method using rice husk silica (RHS), and transformed to proton form (HZSM-5) by ion exchange with  $\text{NH}_4\text{NO}_3$  and calcination. Both forms were modified by desilication with NaOH to produce hierarchical zeolite. The presence of mesopores in the zeolite could facilitate diffusion of the starting reagents to active sites and improve catalytic performance for phenol hydroxylation. The parent and modified ZSM-5 zeolites were used as supports for iron (Fe) catalyst with loading of 5 wt. %. From X-ray diffraction (XRD), ZSM-5 structure was observed in all zeolite and supported Fe catalysts. The peaks of Fe species were not observed in XRD pattern suggesting a good dispersion. The oxidation number of the iron supported on ZSM-5 zeolite was +3, as determined by X-ray absorption near edge structure (XANES) spectroscopy. Transmission electron microscopy (TEM) images of all catalysts displayed well-defined crystalline structure, and  $\text{Fe}_2\text{O}_3$  particles were observed in some catalysts. After desilication, results from nitrogen ( $\text{N}_2$ ) adsorption-desorption analysis confirmed the presence of mesopores with a broad range of pore size. After loading with Fe, all catalysts showed lower surface area. The Fe on desilicated ZSM-5 (5Fe/HZSM-5(D)) gave the fastest reaction and the highest conversion because Fe was well dispersed on the support with the highest surface area. However, the selectivity was not improved and the products observed were catechol and hydroquinone with molar ratio of 2:1.

**Key words** ZSM-5; Rice husk Silica; Hierarchical zeolite; Iron; Phenol hydroxylation

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## Preparation of Protic Ionic Liquid/Polyvinylpyrrolidone Composites with Enhanced Hydrophobicity

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Hydrophobic surfaces have recently gained attentions from several industries due to various potential applications. To overcome the static charge accumulation, such surfaces with good electrical conductivity are needed. The introduction of ionic liquids with a certain degree of hydrophobicity into polymer provides the desired conductivity. In this report, several protic ionic liquids (PILs) have been prepared from reactions between Brønsted acids and Brønsted bases. Simple and low cost neutralization reactions between these organic acids and bases produced PILs with high conductivity (up to  $3.36 \text{ mS cm}^{-1}$ ) at room temperature. The obtained PILs were characterized by  $^1\text{H-NMR}$  spectroscopy and their thermal stabilities were studied by thermogravimetric analysis. Several PILs including triethylammonium benzoate with potentially high hydrophobicity were then selected for the composite fabrication. Polymer composites of polyvinylpyrrolidone (PVP) with enhanced hydrophobicity have been prepared with various amounts of the selected PILs. Water contact angles of PVP/PIL composites were measured to evaluate the enhanced hydrophobicity. The surface of PVP without PIL shows poor hydrophobicity with the water contact angle of  $65.93^\circ$ . Upon the addition of PILs, the PVP composite with 20% of triethylammonium benzoate exhibits the largest water contact angle of  $117.4^\circ$ .

**Keywords** Protic ionic liquid; Hydrophobicity; Polymer composite

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## Transesterification of Crude Palm Oil into Biodiesel Catalyzed by Highly Active Calcium Oxide-based Catalysts

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Using high loading of free fatty acid in crude palm oils under base-catalyzed transesterification reaction for the production of biodiesel instead of the favored high-cost refined palm oils is quite challenged. In this work, the high surface area of calcium oxide and calcium silicate nanoparticles with various ratio of Ca to Si was prepared by sol-gel process in the presence of PVP stabilizer. Their particle sizes of obtained nanocatalysts are in the range of 20-50 nm. The basic strength for both catalysts, estimated by Hammett indicator method, was found to be  $15 < H_a < 18.4$ . The catalytic performance for the biodiesel production was investigated *via* transesterification of crude palm oil under various reaction conditions. Calcium oxide nanocatalysts showed the highest catalytic activity. The conversion of triglycerides into methyl esters (biodiesel) of 98% was achieved in an hour with only 1 percent of catalyst at 60°C and 8:1 ratio of methanol to oil. Calcium silicate nanocatalysts showed the lower reaction kinetic than calcium oxide, however nearly complete conversion can be achieved in 2 hour. Further investigation showed that the catalytic performance of physical mixing of nano-calcium oxide and mesoporous nano-silicon dioxide was higher than pure calcium silicate, and that the formation of soap decreased.

**Keywords** CaO-based nanocatalyst; biodiesel production; crude palm oil

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