Chemical Sensing and Catalytic Properties of Water-Stable Metal-Organic Frameworks Constructed from Dicarboxylate Ligands

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Thesis Title:	**Chemical Sensing and Catalytic Properties of Water-Stable Metal-Organic Frameworks Constructed from Dicarboxylate Ligands**
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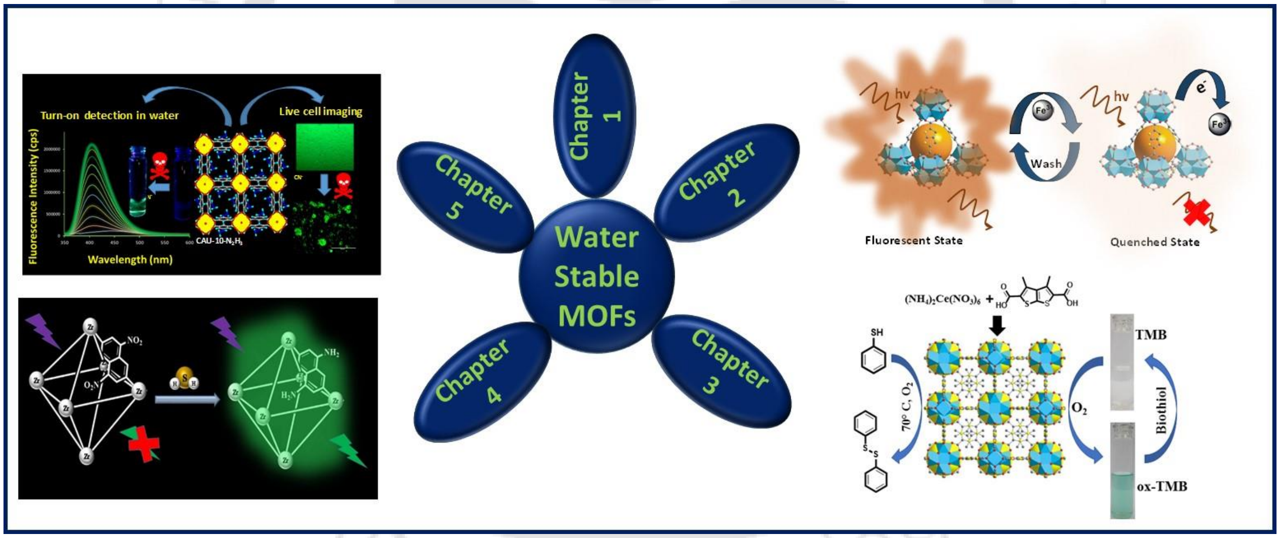
Thesis Overview:



Chapter 1 describes the design principles of water-stable MOFs and their applications in adsorption, sensing and catalysis. The construction of secondary building units (SBUs) of MOFs with an inert metal ion (Cr(III), Al(III) or Fe(III)) is a well-accepted strategy for the synthesis of water-stable MOFs. The metal-ligand coordination bond strength also plays a key role for the hydrolytic stability of MOFs. Pearson's hard/soft acid/base principle can be a rough approximation for the metal-ligand bond strength. Carboxylate-based ligands can be regarded as hard bases and they form strong coordination bonds with high valent metal ions e.g. Cr(III), Al(III), Fe(III), Zr(IV), Hf(IV), Ce(IV), Ti(IV), which can act as hard acids. The hydrolytic stability of a MOF material also largely depends on the coordination geometry, extent of orbital overlap, high connectivity of metal cluster and steric factors. The high connectivity of metal cluster in the framework provides high thermal and chemical stability. Use of hydrophobic ligands during the synthesis is a simple and single-step protocol for the synthesis of hydrophobic and water-stable MOFs. Other than direct synthesis, post-synthetic modification also imparts hydrophobicity in the MOF, which increases the hydrolytic stability. The water-stable MOFs have been employed as high-capacity adsorbents of gases, water, organic molecules, oil, cation, anion, etc. The detection of targeted analytes present in water can be achieved by water-stable fluorescent MOFs. The hydrolytically stable MOFs have been also applied as reusable heterogeneous catalysts for various industrially relevant organic reactions.

Chpater 2 describes the synthesis of four isoreticular thienothiophene-based Zr(IV) MOF materials (**1′**, **2′**, **3′** and **4′**) under solvothermal conditions. All the MOFs possess the UiO-66 (UiO = University of Oslo) framework topology and contains $[Zr_6O_4(OH)_4]^{12+}$ building units (Figure 1). The μ_3-O and μ_3-OH groups occupy the triangular faces of the Zr_6 octahedron. Every Zr atom is coordinated with eight O atoms, forming a square antiprismatic coordination environment. The 3D, cubic framework is constructed by the interconnection of the $[Zr_6O_4(OH)_4]^{12+}$ units with the -CO_2 groups of twelve ligands. The hydrophobicity and fluorescence properties of all the MOF compounds have been tuned in a systematic fashion by attaching methyl and phenyl groups to the thienothiophene-based ligands. As verified by the fluorescence titration experiments, all the MOF materials featured selective, fast, and sensitive sensing of Fe^{3+} ions in water through the fluorescence quenching mechanism (Figure 2). The quenching efficiencies of the materials towards Fe^{3+} ions decreased in the order: **4′** (98%) > **3′** (96%) > **2′** (91%) > **1′** (86%). This trend in the quenching efficiency of the compounds can be correlated with the electron density available in their frameworks. Thorough experimental studies indicate that the transfer of electrons from the π-conjugated, electron-rich thienothiophene-based frameworks to the half-filled 3d orbitals of Fe^{3+} ions accounts for the fluorescence quenching of MOF compounds.

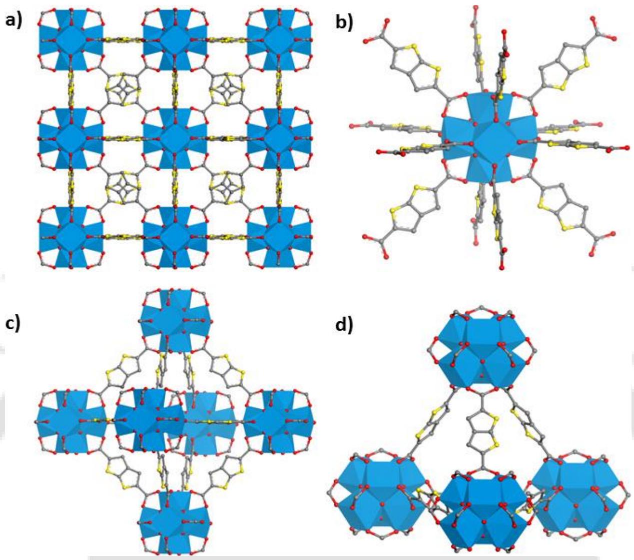


Figure 1. (a) Cubic 3D framework structure of **1** with Zr_6 node. (b) Node connectivity for the framework structure of **1**. Views of the (c) octahedral and (d) tetrahedral cages. Colour codes: Zr, blue polyhedra; C, grey; O, red; S, yellow).

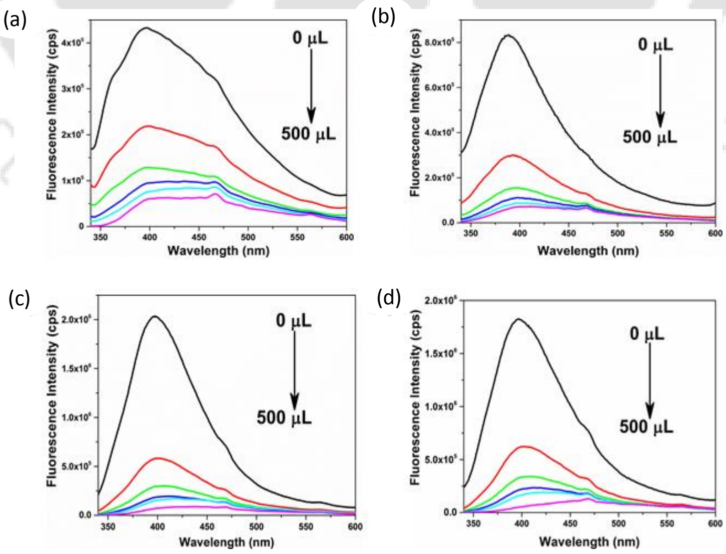


Figure 2. Quenching of fluorescence intensity with gradual addition of Fe^{3+} solution to a 3 mL aqueous suspension of **1′** (a), **2′** (b), **3′** (c) and **4′** (d).

In addition, molecular logic gates were designed by employing the MOFs for distinguishing between Fe^{3+} and Fe^{2+} ions. Overall, high photostability and reusability in Fe^{3+} sensing as well as the ability to discriminate between Fe^{3+} and Fe^{2+} ions through logic operations make the MOFs suitable for real-life applications.

Chapter 3 describes the solvothermal synthesis and characterization of a Ce(IV)-based MOF (**5**) material incorporating 3,4-dimethyl thieno[2,3-b]thiophene-2,5-dicarboxylic acid. The XPS study reveals the presence of both Ce(III) and Ce(IV) ions in the framework.

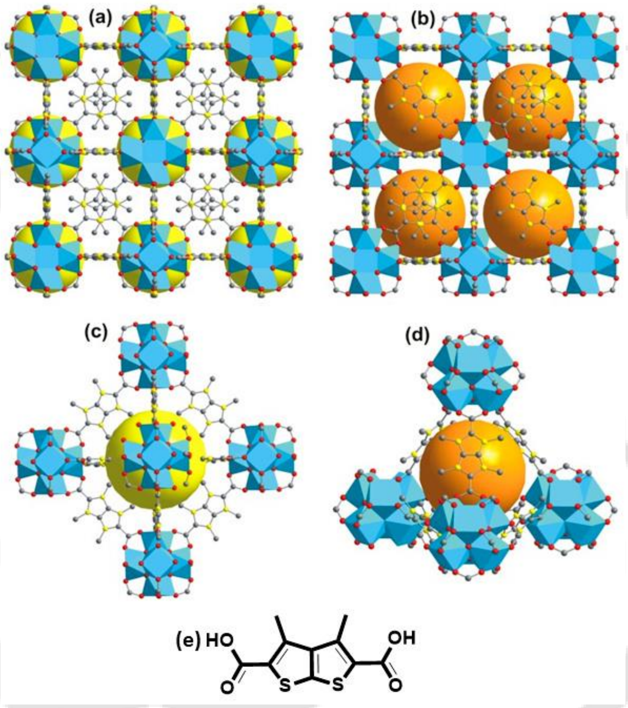


Figure 3. Cubic 3D framework structure of **5** in ball-and-stick representation. (a, b) Depiction of octahedral (yellow spheres) and tetrahedral (orange spheres) cages. (c, d) are the magnified views of (a, b), respectively. (e) Structure of the H_2DMTDC ligand. Colour codes: Ce, blue polyhedra; C, grey; O, red; S, yellow.

The cubic framework structure (Figure 3) of the compound comprises hexanuclear cluster cores having a $[Ce_6O_4(OH)_4]^{12+}$ composition. In these cluster cores, the six cerium atoms are situated at the corners of an octahedron. The eight faces of each octahedron are bridged by the O atoms of μ_3-O and μ_3-OH groups, which are arranged in an alternating fashion. Eight O atoms are coordinated with each Ce atom. The latter has a square antiprismatic geometry in which the O atoms from the carboxylate, μ_3-O and μ_3-OH groups occupy the square faces.

Remarkably, the activated compound (**5′**) mimics the catalytic activity of biological oxidase enzymes due to the existence of redox-active cerium atoms in the framework. The excellent oxidase-like catalytic properties of the material were demonstrated by employing characteristic chromogenic peroxidase substrates: TMB and AzBTS. Based on the oxidase-mimicking activity of MOF, a colorimetric sensing platform for biothiols in NaAc buffer (0.2 M, pH = 4) was established. It can be seen from Figure 4 that the absorbance of ox-TMB decreased dramatically upon gradual addition of 0.5 mM solutions of cysteine. The sensing ability of biothiols by the MOF was employed to detect cysteine in human blood plasma. A significant heterogeneous catalytic performance of the mixed valence state Ce-MOF was also observed in the oxidation of thiol compounds using molecular oxygen (Scheme 1). The hot filtration experiments confirmed the heterogeneity of the oxidation catalysis reaction. The conversion of thiophenol observed in the 1st, 2nd, 3rd and 4th cycles after 12 h corresponded to 100%, 98%, 97% and 96%, respectively, which confirms the recyclability of **5′**.

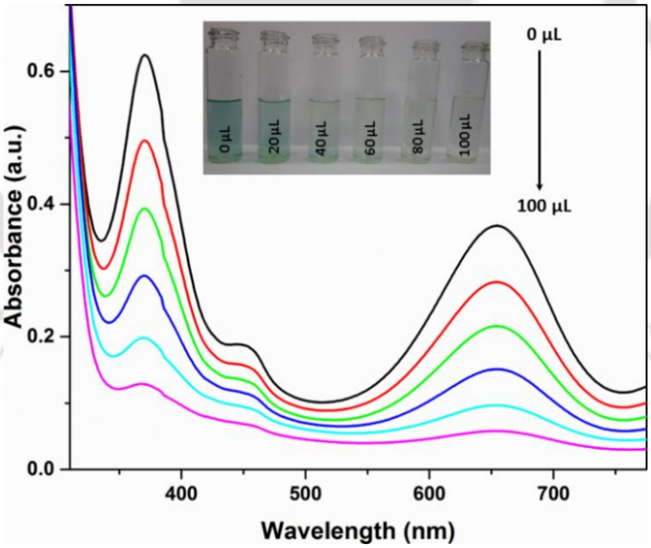
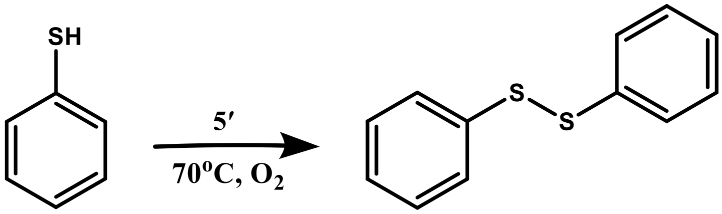
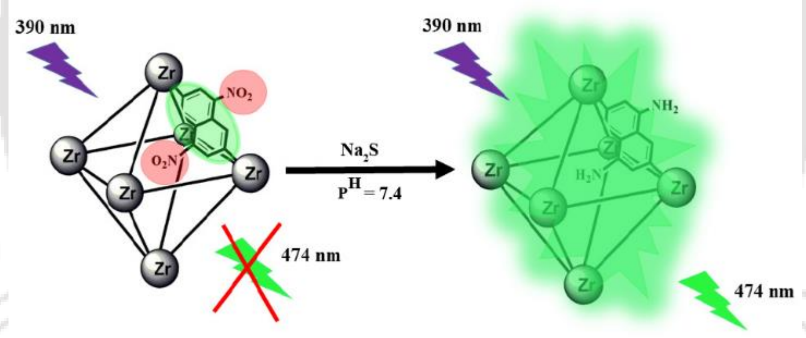


Figure 4. Change in the absorption spectrum of ox-TMB upon gradual addition of 0.5 mM cysteine solution in NaAc buffer (0.2 M, pH = 4). Inset: corresponding change in color of the ox-TMB solution.



Scheme 1. Oxidation of thiophenol to 1,2-diphenyldisulfide in presence of catalyst **5′** and molecular oxygen.

Chapter 4 describes the synthesis, characterization of dinitro-functionalized Zr(IV)-based DUT-52-$(NO_2)_2$ MOF (**6**) (DUT = Dresden University of Technology). The activated material (**6′**) acts as a colorimetric and fluorogenic turn-on probe for the sensing of H_2S under physiological conditions (HEPES buffer, pH = 7.4, temperature = 37 °C) (Scheme 2). As confirmed by the steady-state fluorescence titration experiments, the MOF compound features significant capabilities for the highly selective and sensitive (detection limit: 20 µM) detection of H_2S.



Scheme 2. Sensing of H_2S sensing by **6′** under physiological conditions (HEPES buffer, pH = 7.4, temperature = 37 °C) through fluorescence turn-on mechanism.

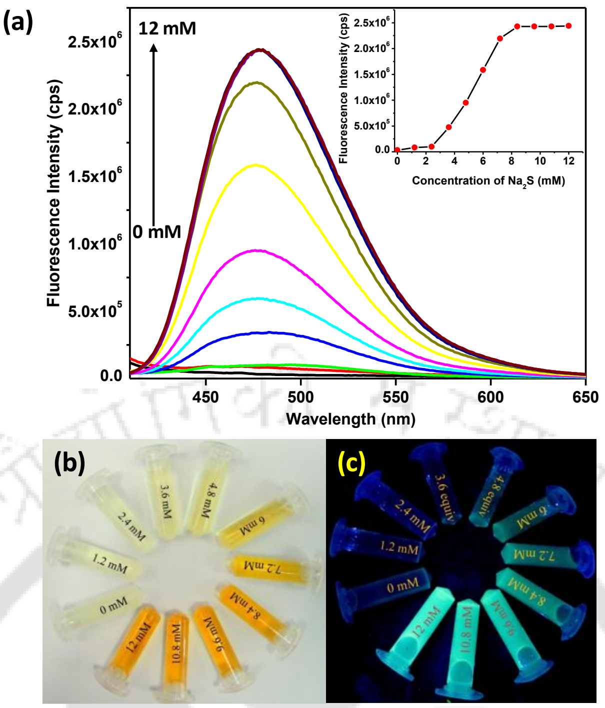


Figure 5. (a) Fluorescence turn-on response of **6′** (0.04 M) with increasing concentrations of Na_2S. Concentration-dependence of the emission intensity (monitored at 474 nm) is shown in the inset. The corresponding naked-eye colorimetric responses of **6′** towards H_2S under (b) day light and (c) UV light are also displayed.

The presence of two nitro functional groups per $H_2NDC\text{-}(NO_2)_2$ ligand completely quench the fluorescence of the naphthalene moiety in dinitro-functionalized Zr-based DUT-52 (Figure 5a). The corresponding diamino-functionalized MOF compound, formed through H_2S-mediated reduction, is expected to be more fluorescent than the dinitro-functionalized material. Remarkably, the compound exhibited visually detectable colorimetric and fluorogenic responses towards H_2S under day light as well as under UV irradiation (Figure 5b and 5c). In addition, the probe could be used for the detection of H_2S in human blood plasma and as well as living cells.

Chapter 5 describes the synthesis and systematic characterization of a hydrazine-functionalized Al(III) MOF namely CAU-10-N_2H_3 (**7**). The framework structure of **7** is presented in Figure 6. As revealed from the figure, the framework of CAU-10-N_2H_3 is formed by the interconnection of cis-corner sharing [AlO_6] octahedra with the hydrazine-functionalized isophthalate ligands. This structural connectivity leads to the formation of helical chains. Two adjacent helices are related by a mirror plane.

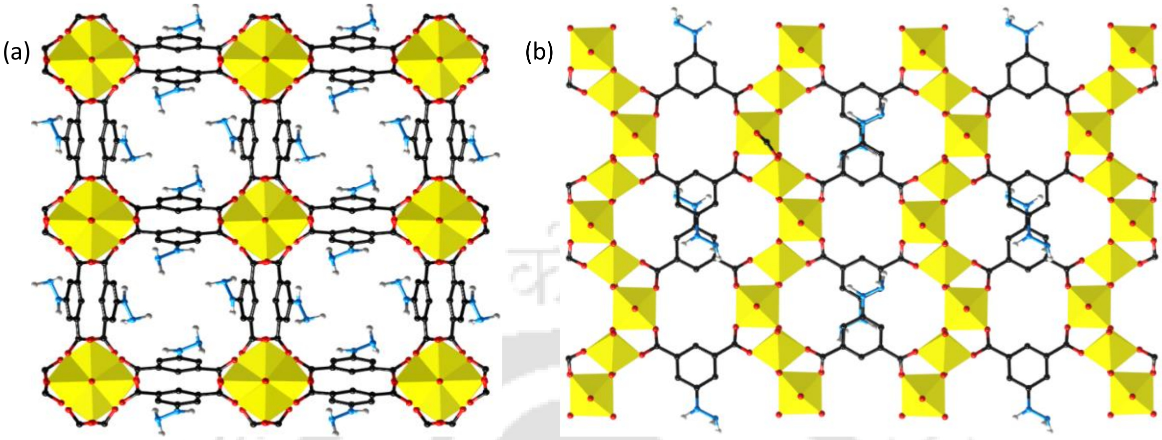


Figure 6. The simulated structure of the framework of CAU-10-N_2H_3 (**7**) compound (a). Hydrogen atoms have been omitted from phenyl ring of the structural diagram for clarity. Helical arrangement of [AlO_6] octahedra in the framework of CAU-10-N_2H_3 as seen along the b-axis (b). Colour codes: C, black; O, red; N, blue; Al, yellow polyhedra; H, white.

The activated material **7′** is capable of sensing CN^- ions even in the presence of other competitive anions present in water (Figure 7). The appearance of green fluorescence under UV light upon cyanide addition makes this material a naked-eye fluorescent sensor for CN^- ions in aqueous medium. The cyanide induced deprotonation of the acidic -NH proton present in hydrazine-functional group was confirmed by ^{1}H NMR titration experiment. This deprotonation leads to the fluorescence turn-on signal of the MOF probe. A very low detection limit of 0.48 μM was obtained for this MOF, which is lower than the allowable cyanide concentration (2 μM) in drinking water according to the WHO. The live cell imaging experiments with non-toxic Al(III) MOF clearly establish that the MOF is capable of intracellular CN^- ions.

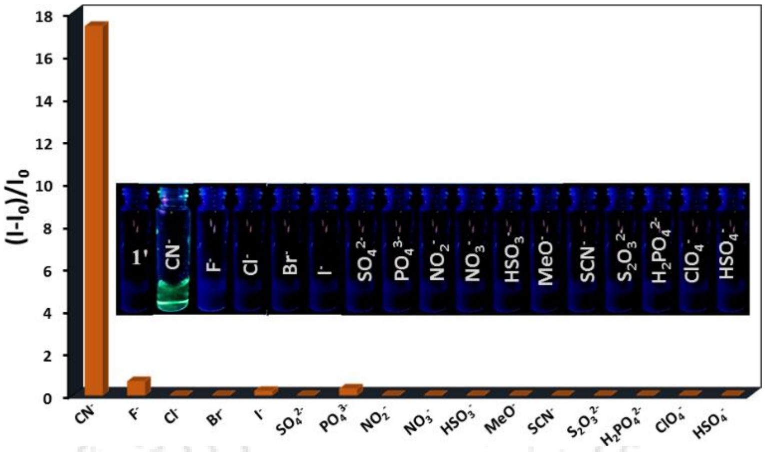


Figure 7. Relative fluorescence enhancement behaviour of **7′** towards addition of different anions. Inset: naked-eye fluorogenic response of **7′** towards different anions.