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A Mini Review on Recent Advances in Luminescent Coordination Polymers as Sensors for Dichromate Detection

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Abstract. The detection of hazardous pollutants, particularly chromium(VI) species such as dichromate ($Cr_2O_7^{2-}$), remains a significant environmental and public health challenge due to their toxicity and carcinogenic nature. Conventional analytical techniques, while highly accurate, suffer from drawbacks such as high cost, complexity, and the need for specialized infrastructure, making real-time and on-site monitoring difficult. Luminescent coordination polymers (LCPs) have emerged as promising alternatives for Cr(VI) detection, offering benefits like tunable luminescence, high discernment, and fast response. This review explores recent advances in LCP-based sensors, emphasizing design principles, synthesis strategies, and fluorescence quenching mechanisms, including electron transfer, energy transfer, and the inner filter effect. The role of metal centers and organic ligands in enhancing sensing performance is examined, alongside the impact of structural modifications, nanotechnology-driven innovations, and composite materials. Additionally, we discuss the integration of computational modeling and machine learning in optimizing sensor performance. Challenges related to stability, selectivity, and real-world applicability are addressed, along with potential strategies to improve sensor robustness under diverse conditions. Finally, we outline future directions, including hybrid materials, miniaturized platforms, and green chemistry approaches, underscoring the potential of LCP sensors for sustainable and efficient Cr(VI) detection. This review provides a comprehensive perspective on the progress, challenges, and future outlook for LCP-based sensors in environmental monitoring.

1 Introduction

The contamination of water by dichromate ions, largely from industrial effluents, poses significant environmental and health risks. Chromium(VI) species like dichromate ($Cr_2O_7^{2-}$) and chromate (CrO_4^{2-}) are highly toxic, carcinogenic, and mutagenic, contributing to severe pollution in water sources [1]. Industries such as leather tanning, electroplating, and textile dyeing are key sources of this pollution [1, 2]. These ions can easily contaminate groundwater and affect both aquatic ecosystems and human health, leading to respiratory issues, liver and kidney damage, and genetic mutations [1]. Traditional methods for detecting dichromate ions, like inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectroscopy (AAS), and high-performance liquid chromatography (HPLC), are accurate but costly and require specialized equipment [3]. In contrast, optical sensors based on luminescent coordination polymers (LCPs) have gained attention due to their rapid response, high selectivity, and ease of use. These metal-organic frameworks (MOFs) exhibit unique photophysical properties and have tunable luminescence, making them ideal for sensing applications [4]. LCPs selectively detect Cr(VI) species through fluorescence quenching or enhancement, providing a viable alternative to traditional methods[5]. Developments in computational chemistry, nanotechnology, and materials science have led to the fabrication of LCPs with enhanced sensitivity and stability. For instance, density functional theory (DFT) helps predict interactions between LCPs and analytes, while nanocomposites improve sensor performance [6]. These efforts have accelerated the development of next-generation sensors for environmental and industrial safety. Given growing concerns about water contamination and the limitations of current detection methods, developing efficient, selective, and cost-effective sensors for Cr(VI) is crucial. This review highlights recent advances in LCP-based sensors, their interaction with dichromate ions, and the challenges remaining in this field, while also suggesting future research directions to improve their practicality and commercial viability.

2. Design and Synthesis of LCPs for Dichromate Sensing

The design of luminescent coordination polymers (LCPs) for dichromate sensing requires careful selection of metal centers and organic ligands to achieve the desired structural and photophysical properties. Recent studies have focused on using d^{10} metal ions like Zn^{2+} and Cd^{2+}, combined with conjugated organic ligands, to create frameworks with improved luminescence and stability [4]. For instance, Parmar et al. synthesized Zinc and Cadmium LCPs using two ligands, which showed high hydrolytic stability and strong luminescent responses to dichromate ions [4]. The inclusion of both flexible and rigid linkers in these LCPs has been shown to impact the electron transfer dynamics and ligand-metal interactions, enhancing sensing performance [7]. In addition to Zn and Cd, lanthanide-based LCPs have been explored due to their sharp emission bands, long lifetimes, and resistance to quenching. Eu(III)-based LCPs have shown excellent selectivity for Cr(VI) ions through energy transfer mechanisms that lead to distinct fluorescence quenching [8]. Tb(III)-based LCPs also exhibit strong emission intensities that decrease upon interaction with $Cr_2O_7^{2-}$, indicating their potential as sensitive sensors [9]. Advancements in synthetic strategies, such as hydrothermal, solvothermal, and microwave-assisted methods, have improved the crystallinity, porosity, and sensing capabilities of LCPs [9]. Functionalization of LCPs with electron-rich moieties like nitrogen-containing heterocycles and π-conjugated systems further strengthens interactions with dichromate ions, improving sensitivity [9]. By optimizing coordination environments and ligand designs, researchers have developed LCPs with enhanced selectivity, stability, and response times, advancing their practical application in environmental monitoring [9].

3. Sensing Mechanisms of LCPs for Dichromate Detection

The sensing mechanisms of LCPs for dichromate detection primarily rely on fluorescence quenching, which occurs due to various interactions between the analyte and the luminescent framework. Several key mechanisms contribute to this sensing process, including electron transfer, energy transfer, and the inner filter effect. Electron Transfer[10]: One of the most common quenching pathways involves electron transmission from the excited-state LCP to the dichromate ion. Due to the strong oxidizing nature of Cr(VI) species, they can accept electrons from the LCP framework, resulting in a decrease in fluorescence intensity. Energy Transfer: Non-radiative energy transfer between the LCP and dichromate ions can also lead to quenching. This occurs when the emission energy of the excited LCP overlaps with the absorption energy of Cr(VI), facilitating an efficient energy transfer process. Inner Filter Effect (IFE)[10]: The strong absorption of Cr(VI) species, particularly in the UV-visible region, can affect with the excitation or emission wavelengths of the LCP sensor. This absorption reduces the observed fluorescence intensity, making IFE a dominant quenching mechanism in many LCP-based sensing systems. Dynamic and Static Quenching: Depending on the nature of the interaction, fluorescence quenching can be classified as dynamic (collisional) or static (complex formation). In dynamic quenching, interactions between LCPs and Cr(VI) ions occur in the excited state, whereas static quenching involves ground-state complexation, leading to fluorescence suppression. Enhancement Mechanisms: While most LCP-based sensors rely on fluorescence quenching for Cr(VI) detection, certain modifications in framework design and ligand incorporation can result in fluorescence enhancement. Ligand-to-metal charge transfer (LMCT) and antenna effects in lanthanide-based LCPs can improve signal intensity, offering alternative sensing strategies. The combination of these mechanisms allows for the development of highly selective and sensitive LCP sensors for dichromate detection[10].

4. Recent advances in Coordination polymers as fluorescent sensor for dichromate

Luminescent coordination polymers (LCPs) have shown great potential as sensors for sensing toxic dichromate ($Cr_2O_7^{2-}$) ions due to their high sensitivity, selectivity, and adjustable fluorescence properties. Recent advances, especially in Cd(II)-based frameworks, have demonstrated effective fluorescence quenching via the inner filter effect (IFE), enabling fast and reliable Cr(VI) detection in water. The use of nitrogen-donor co-ligands like 2,2'-bipyridine and 1,10-phenanthroline enhances luminescence stability, ensuring selective ion recognition as shown in Figure 1. Additionally, a turn-off/turn-on fluorescence mechanism using 2-hydroxybenzoic acid improves sensor reusability. LCP sensors have been successfully applied in environmental water testing, with portable test strips offering a cost-effective solution. However, challenges remain in stability across pH variations, selectivity in complex samples, and large-scale synthesis. Future research should focus on hybrid materials, computational design, and smart sensing integration to enhance detection limits, durability, and eco-friendly synthesis for broader environmental and industrial applications [11].

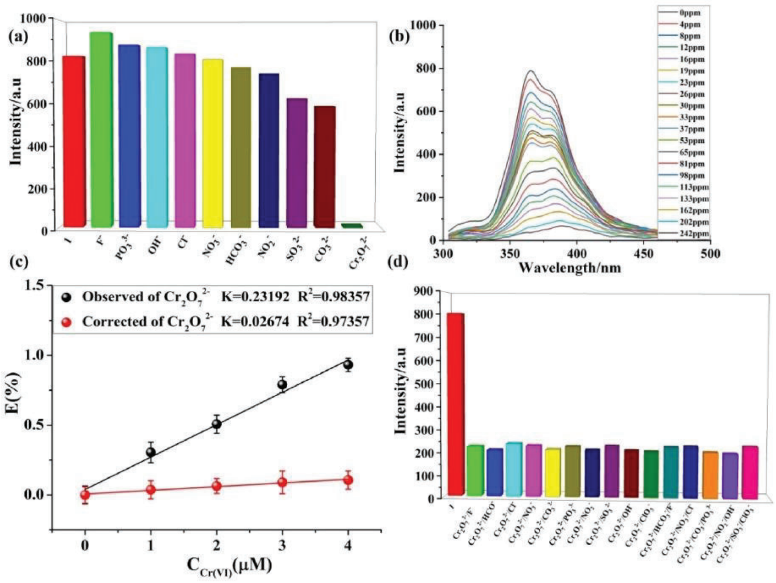

Figure 1. (a) Bar graph showing the decrease in photoluminescence intensity of CP 1 with various anions. (b) Fluorescence spectra of CP 1 upon stepwise addition of 1 mM $Cr_2O_7^{2-}$ (λex = 300 nm). (c) Quenching efficiency (E%) calculated from fluorescence intensity changes at different $Cr_2O_7^{2-}$ concentrations. (d) Interference study assessing CP 1's selectivity against other anions. Reprinted with approval [11].

$[Cd(H_2dhbdc)(NI\text{-}mbpy\text{-}34)_2]_n$ (1) is a Fluorescent cadmium(II) coordination polymer that has been synthesized, characterized, and sensed by fluorescence for the selective detection of Al^{3+}, Cr^{3+}, and Cr(VI) oxyanions ($Cr_2O_7^{2-}$ and CrO_4^{2-}). Hydrothermally synthesized, it exhibits high luminescence in aqueous conditions and develops a stable 2D grid-like sql structure that is modified by pH and solvent. The sensor has a high selectivity, turning on for Al^{3+} and Cr^{3+} and turning off for $Cr_2O_7^{2-}$ and CrO_4^{2-}. The inner filter effect (IFE) and energy transfer are the primary causes of the quenching. The Stern-Volmer equation was used to estimate the detection limits, which were 12.43 μM for CrO_1^{2-} and 5.85 μM for CrO_4^{2-} as revealed in Figure 2. Studies on anti-interference verified its efficacy in intricate matrices, indicating its potential as a multipurpose fluorescence sensor for environmental monitoring of chromium contaminants[12].

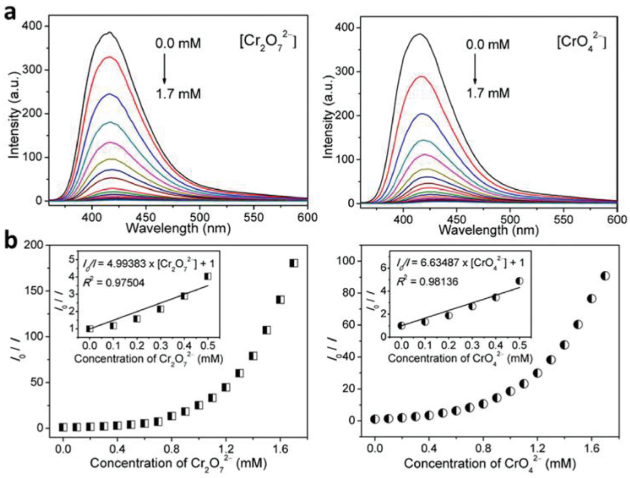

Figure 2. (a) CP 1's luminescence spectra in water at various concentrations of CrO_4^{2-} and $CrO_2O_7^{2-}$. (b) I_0/I ratio against anion concentration in a Stern-Volmer plot, with an inset illustrating the linear fit at low $Cr_2O_7^{2-}$ and CrO_4^{2-} levels. Conditions of the experiment: λ_ex = 350 nm, λ_em = 414 nm. Reprinted with permission [12].

Xiamei Zhang and coauthors synthesized Cd(II) coordination polymer (CP 1) for $Cr_2O_7^{2-}$ and CrO_4^{2-} detection in aqueous media. Figure 3 shows that the polymer exhibits strong luminescence, selectively quenched by Cr(VI) oxyanions via the inner filter effect (IFE), where anions absorb excitation energy, reducing fluorescence intensity. Stern-Volmer analysis shows a linear response at low Cr(VI) concentrations, indicating high sensitivity with micromolar detection limits. The sensor demonstrates excellent selectivity with minimal interference from other anions and was successfully tested in environmental water samples. Future enhancements could involve ligand modifications for better electron transfer, nanomaterial integration for lower detection limits, and development of portable sensing platforms for real-time monitoring [13].

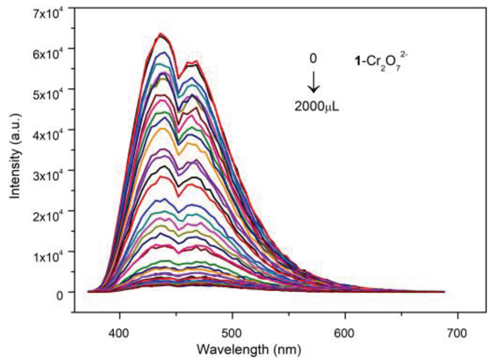

Figure 3. Luminescence emission spectra of CP 1 in aqueous suspension at different $Cr_2O_7^{2-}$ concentrations, showing fluorescence quenching with increasing analyte levels. Reprinted with approval [13].

Two Zn(II)-based mixed-ligand coordination polymers (CP-1 and CP-2) for multi-responsive fluorescence sensing were synthesized and studied by Dan Wang and colleagues. Strong luminescence was demonstrated by these 2D frameworks, which were made by solvothermal techniques utilizing 1,4-di(imidazole-1-yl) naphthalene (DIN) and 1,3,5-benzenetricarboxylic acid (H_3BTC). Under various excitation wavelengths

(225 and 290 nm) as shown in Figure 4, CP-1, which has an emission peak at 350 nm, responded selectively to $Cr_2O_7^{2-}$, I^-, nitenpyram (NTP), and imidacloprid (IMI). With detection limits in the sub-micromolar range and Stern-Volmer quenching constants of 1.08×10^4 M^{-1} (225 nm) and 1.21×10^4 M^{-1} (290 nm), fluorescence quenching studies demonstrated exceptional sensitivity and selectivity for $Cr_2O_7^{2-}$. The inner filter effect (IFE) and potential fluorescence resonance energy transfer (FRET) were the primary causes of the quenching. Excellent stability and reusability were displayed by the sensor, which maintained its fluorescence after many. This study highlights the potential of Zn(II)-based CPs as cost-effective, selective, and reusable fluorescent sensors for detecting toxic anions and pesticides in environmental monitoring [14].

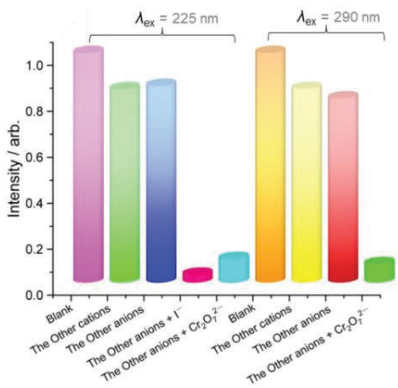

Figure 4. Competitive fluorescence quenching experiments show that CP-1 selectively recognizes I^- and $Cr_2O_7^{2-}$, effectively distinguishing these anions from other potential interferents. Reprinted with permission from [14].

Another work present a Zn(II) coordination polymer, $Zn_2(BDC)_2(dbpt)_2$ (1), designed for dual functions: detecting Cr(VI) anions and treating glomerulus nephritis. The polymer, synthesized solvothermally, shows strong fluorescence stability in water, enabling selective Cr(VI) detection with sub-ppm sensitivity. Fluorescence quenching exposed in Figure 5, occurs through inner filter effect (IFE) and ligand-to-ligand charge transfer (LLCT).

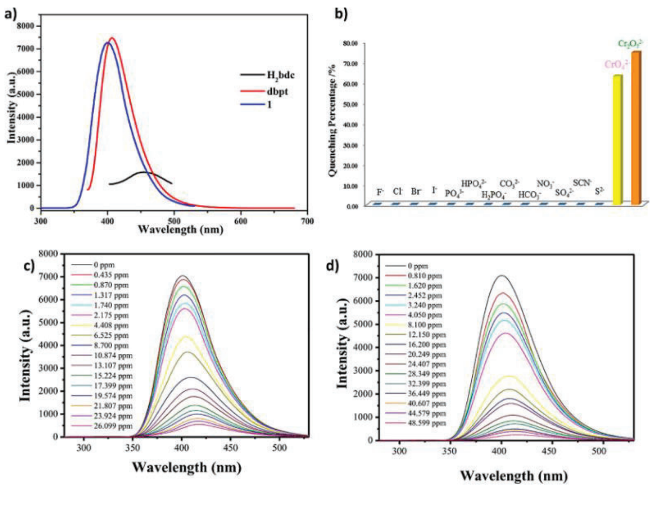

Figure 5. (a) Solid-state emission spectra of CP-1 and its ligands. (b) CP-1's fluorescence quenching efficiency at [An⁻] = 0.075 mmol/L (λ_ex = 272 nm) after adding different anions to a water suspension.

(c) CP-1's fluorescence titration using CrO_4^{2-}. (d) CP-1's fluorescence titration using $Cr_2O_7^{2-}$. Reprinted with permission from [15].

It also reduces reactive oxygen species and inflammatory cytokines in glomerular cells, as shown by ELISA assays, suggesting anti-inflammatory activity. Molecular docking hints at NF-κB binding, pointing to its potential as both an environmental sensor and therapeutic agent[15].

A recent study by Huijun Li and colleagues describes a multifunctional fluorescence chemosensor using a terbium-based metal-organic framework (Tb-MOF). The MOF, prepared using post-synthesis strategy and loaded with a fluorophore molecule, enables the sequential detection of 2,6-pyridinedicarboxylic acid (DPA) and dichromate anions ($Cr_2O_7^{2-}$). The sensor emits strong green fluorescence from Tb^{3+} ions, while the fluorophore provides additional red emission. It operates via a turn-off mechanism when exposed to bacterial spores, followed by further quenching with dichromate anions, shown in Figure 6, for consecutive detection. The system offers real-time, ratiometric fluorescence response, making it a sensitive and selective tool for detecting biological and environmental contaminants. Additionally, Ru(II)@HPU-25 is highlighted as a multifunctional sensor capable of detecting multiple pollutants, maintaining excellent selectivity for $Cr_2O_7^{2-}$ after DPA detection [16].

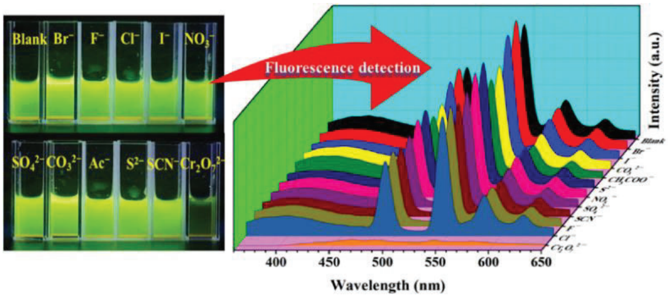

Figure 6. shows how the fluorescence intensity of DPA@Ru(II)@HPU-25 is affected by 40 μM of various anions. Reprinted with permission from [16].

Yan-Ning Wang and colleagues describe the preparation, characterization, and fluorescence detection properties of a new coordination polymer (Mn-CP) made using a semi-rigid tricarboxylate acid ligand. The 3D network of the polymer is stabilized by coordination interactions between Mn(II) centers and the ligand's carboxylate groups. Fluorescence studies show that Mn-CP exhibits strong luminescence, which is selectively quenched by acetylacetone and dichromate anions ($Cr_2O_7^{2-}$) as shown by Figure 7. The quenching mechanism involves photoinduced electron transfer and inner filter effects. The polymer demonstrates high sensitivity and selectivity for detecting these analytes in water based solutions, enabling a dual-channel fluorescence response [17].

The design and use of ZnMOF-1 and CdMOF-1 as extremely sensitive and selective fluorescence sensors for identifying chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) anions in water are examined in a study by Manpreet Kaur and associates. The inner filter effect and electron transfer between the MOF and chromate species are responsible for the fluorescence quenching mechanism, which causes a noticeable drop in luminescence intensity. According to the study, even when competing anions are present, the Schiff base-modified MOF sensors exhibit good selectivity, low detection limits, and high sensitivity for chromate and dichromate ions (Figure 8). Furthermore, the sensors show promise for environmental monitoring and water quality evaluation by operating well in actual water samples. Additionally, they exhibit good recyclability, maintaining fluorescence intensity across three cycles with few alterations [18].

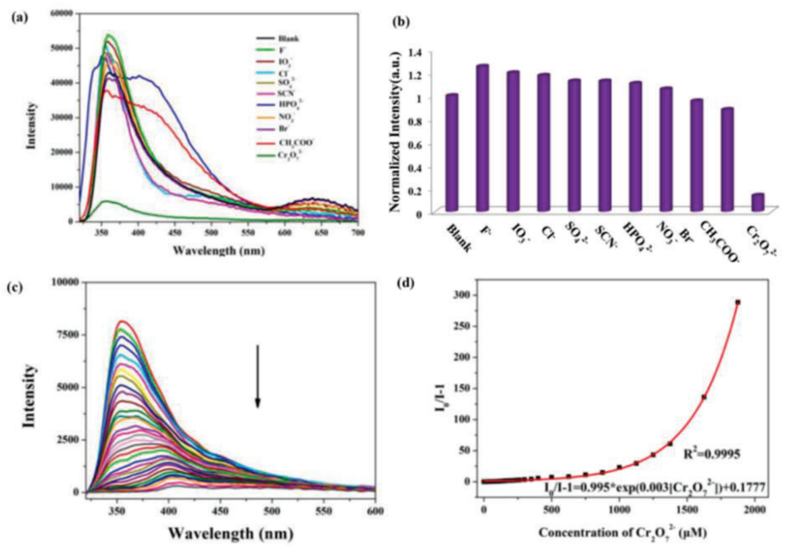

Figure 7. The compound 1 luminescence emissions (a) and relative intensities (b) with various ions added to the aqueous emulsions (0.1 M); the luminescence responses to various concentrations of $Cr_2O_7^{2-}$ in the aqueous emulsions of 1; and the S-V plot for 1 after adding $Cr_2O_7^{2-}$ incrementally (λex = 300 nm). Reprinted with permission from [17].

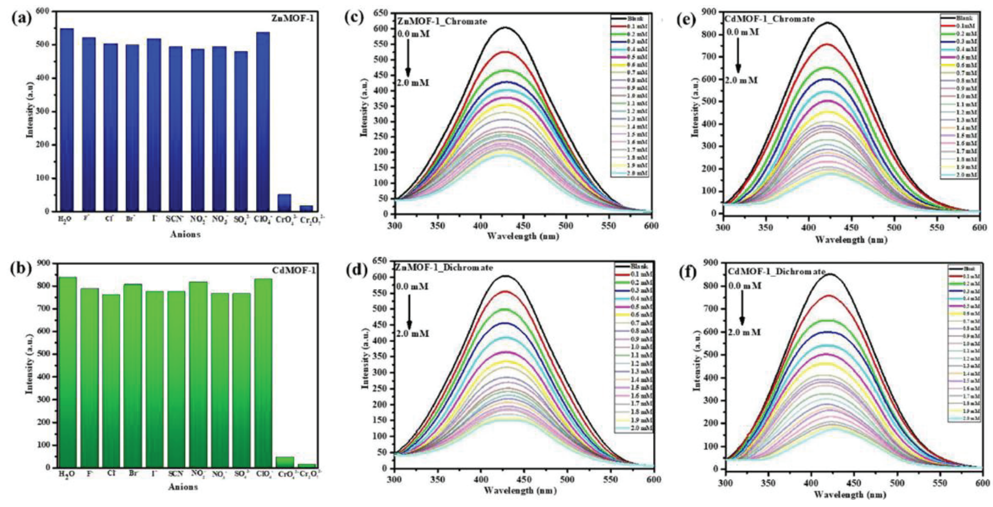

Figure 8. (a, b) ZnMOF-1 and CdMOF-1 (3.0 mg/3 mL) suspended in various aqueous anion solutions suppress fluorescence. (c) Luminescence responses of ZnMOF-1 and CdMOF-1 (3 mg dissolved in 3 mL water) to varying CrO_4^{2-}/$Cr_2O_7^{2-}$ (0 - 2.0 mM) concentrations in water. Reproduced with permission from [18].

The fabrication of Hf-BITD, a hydrolytically stable metal-organic framework, as a fluorescence sensor for the detection of chromate and dichromate anions is described by Xue Wang and associates. Figure 9 shows that even when a variety of cations and anions are present, Hf-BITD exhibits great selectivity and sensitivity for these anions. In aqueous conditions, the sensor's detection limits for CrO_4^{2-} and $Cr_2O_7^{2-}$ are 0.38 nM and 0.33 nM, respectively. These are the lowest levels yet recorded for MOF-based chemosensors and fall below the EPA's permissible limits in drinking water. The inner filter effect, photoinduced electron transfer, and electrostatic interactions are responsible for the MOF's notable dampening effect despite its strong fluorescence characteristics[19].

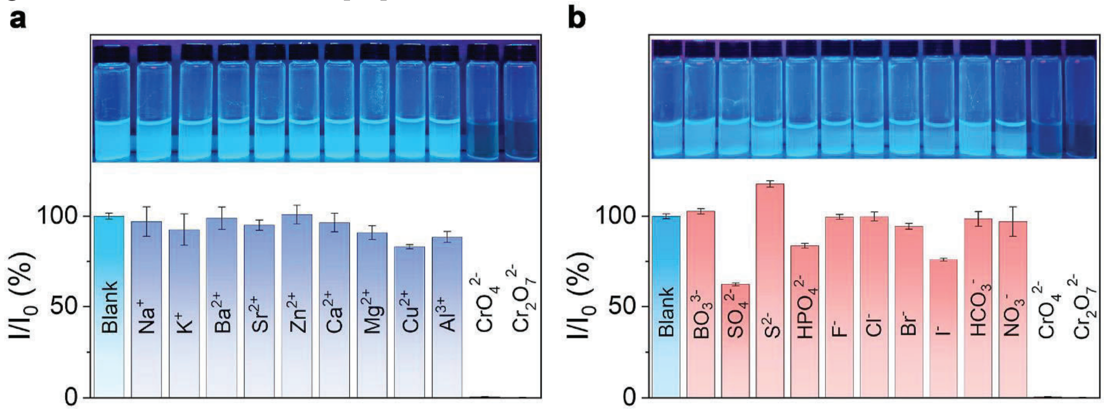

Figure 9. (a) Hf-BITD suspensions in various cation solutions at a concentration of 2 mM are photographed and their luminescence intensities reported. (b) Hf-BITD suspensions in various anion solutions at a concentration of 2 mM are photographed and their luminescence intensities are shown. Reprinted with permission from [19].

The topological control of two new thorium-based MOFs, Th-BCTPE-1 and Th-BCTPE-2, is investigated by Zi-Jian Li and associates. When it comes to identifying chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) anions in aqueous solutions, these MOFs exhibit excellent sensitivity and selectivity (Figure 10). With greater Stern-Volmer constants (Ksv) for both CrO_4^{2-} (2.4×10^5 M^{-1}) and $Cr_2O_7^{2-}$ (4.6×10^5 M^{-1}), Th-BCTPE-1 shows more sensitive luminescence quenching reactions to these anions than Th-BCTPE-2. The study shows that the physiochemical characteristics play a limited effect in determining sensing performance, even if Th-BCTPE-2 is more porous. Mechanisms include the inner filter effect (IFE), charge transfer interactions, and competitive absorption of excitation energy are responsible for the quenching of fluorescence [20].

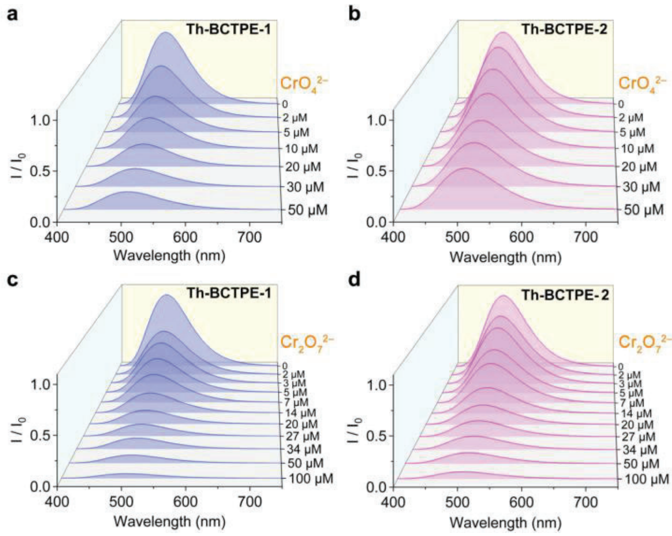

Figure 10. The normalized luminescence spectra of Th-BCTPE-1 at increasing CrO_4^{2-} concentration, Th-BCTPE-2 at increasing CrO_4^{2-} concentration, Th-BCTPE-1 at increasing $Cr_2O_7^{2-}$ concentration, and Th-

BCTPE-2 at increasing $Cr_2O_7^{2-}$ concentration are shown in (a) and (b) respectively. Reprinted with permission from [20].

Conclusion and Future Directions

The growing concerns over chromium(VI) contamination have driven the development of luminescent coordination polymers (LCPs) as promising sensors because of its tunable features, fast response, and high discrimination for Cr(VI) detection. Recent advancements show that LCP-based sensors operate through fluorescence quenching mechanisms, such as electron transfer, energy transfer, and the inner filter effect, to enhance sensitivity toward dichromate ions. However, challenges remain, including structural stability, interference from competing analytes, and performance under real-world conditions. Future research should focus on improving sensor performance through hybrid materials, computational design, sustainable synthesis, and multi-target sensing. Additionally, extensive field testing is needed to validate LCP-based sensors for environmental monitoring and commercial viability. These advancements will drive the development of efficient, sustainable, and selective Cr(VI) detection tools.

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