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Optical chemosensors for environmental monitoring of toxic metals related to Alzheimer's disease†

 Islam M. El-Sewify,^{ab} Ahmed Radwan,^{ab} Nehal H. Elghazawy,^b Wolfgang Fritzsche^c and Hassan M. E. Azzazy^{id*bc}

Alzheimer's disease (AD) is the most common type of dementia and progresses from mild memory loss to severe decline in thinking, behavioral and social skills, which dramatically impairs a person's ability to function independently. Genetics, some health disorders and lifestyle have all been connected to AD. Also, environmental factors are reported as contributors to this illness. The presence of heavy metals in air, water, food, soil and commercial products has increased tremendously. Accumulation of heavy metals in the body leads to serious malfunctioning of bodily organs, specifically the brain. For AD, a wide range of heavy metals have been reported to contribute to its onset and progression and the manifestation of its hallmarks. In this review, we focus on detection of highly toxic heavy metals such as mercury, cadmium, lead and arsenic in water. The presence of heavy metals in water is very troubling and regular monitoring is warranted. Optical chemosensors were designed and fabricated for determination of ultra-trace quantities of heavy metals in water. They have shown advantages when compared to other sensors, such as selectivity, low-detection limit, fast response time, and wide-range determination under optimal sensing conditions. Therefore, implementing optical chemosensors for monitoring levels of toxic metals in water represents an important contribution in fighting AD.

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1. Introduction

Dementia, a neurodegenerative disorder, is characterized by loss of memory, language and problem-solving along with other thinking abilities, which can interfere with a patient's daily life. Dementia can be manifested in different formats such as Alzheimer's Disease, vascular dementia, and Lewy body dementia.¹ Alzheimer's disease (AD) is known to be the most common form of dementia where according to the WHO it represents 60–70% of dementia cases worldwide.² Although AD is commonly diagnosed in aged societies that are older than 65 years old, some cases are considered “early-onset” where symptoms are witnessed as early as 30 years old. For diagnosis, AD is known to have very distinct hallmarks represented in the intracellular neurofibrillary tangles (NFTs) containing the protein tau in a hyper-phosphorylated state and the extracellular plaques containing amyloid beta (A β).^{3–6} Regardless the

distinctive diagnostic markers for AD, unfortunately, the causes behind AD are not quite understood up till now. As such, studying the etiology of AD has been quite a challenging task where it resulted in declaring AD as a multifactorial disorder. Generally, the increase in the incidence of AD along with its progression has been attributed to genetics, environmental factors, and acquired factors such as cerebrovascular diseases, stress, anxiety, and sleep disorders. It can be quite understandable that some risk factors are hardly controllable, still, identifying the controllable ones has become paramount to reduce the AD progression.^{7,8} Latest observations have identified environmental risk factors as key causal players in the progression and onset of AD. Those factors including air pollution, poor diet, contaminated water, and infections can participate in developing AD by initiating oxidative stress and inflammation.^{9,10} Among the well-known environmental risk factors is the prolonged exposure to heavy metals especially those of industrial origin. Such pollutants can be released in the air as fine dust or in water as well as the soil. Those heavy metals have the capacity to initiate the formation of A β plaques and the phosphorylation of the tau protein; thereof, neuronal cell death is a definite outcome.¹¹ In this review, we give a special attention to those heavy metals and how to detect them in water, in hope that these measures act as a protective shield against AD.

^aDepartment of Chemistry, Faculty of Science, Ain Shams University, 11566, Abbassia, Cairo, Egypt

^bDepartment of Chemistry, School of Sciences & Engineering, The American University in Cairo, SSE, Rm #1194, P.O. Box 74, New Cairo 11835, Egypt. E-mail: hazzazy@aucegypt.edu

^cDepartment of Nanobiophotonics, Leibniz Institute for Photonic Technology, Jena 07745, Germany

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allow for simple and quantitative simultaneous detection of multiple toxic metals if used in conjunction with simple colorimeters which reduces the errors caused by sample storage and transportation for analyses by central sophisticated laboratory instruments such as ICP-MS. Optical chemosensors change color upon binding of their immobilized indicators (chromophores) to their target analytes.

3.1. Chemosensor design

Selecting the right carriers is critical for designing chemosensors. In general, many carriers have been used such as zeolites, metal oxides, polymers, metallosupramolecular network, and carbon-based materials.⁶³ Mesoporous silica or metal organic frameworks are generally used as carriers in the preparation of optical chemosensors (Fig. 2).^{64,65} Although, some heavy metals are directly detected *via* ocular property such as luminescence or absorption, there are some targets has no absorption or luminescence property, therefore, optical chemosensors with selective and sensitive optical probe were designed. The designed chemosensor may take various forms such as powder, gels, thin films or nanoparticles. The sensor changes its optical properties in presence of toxic metals.⁶⁶ The detection of common cations in water, cosmetic, or blood is based on complexation between the chromophore and its specific target cation. Therefore, highly selective chromophores with electron donating atoms were prepared and immobilized on carriers *via* covalent, physical, or electrostatic interactions.⁶⁷ Proper selection of mesoporous or MOFs nanomaterials is crucial as it affects mechanical stability of the sensor, dye immobilization, and access of the toxic metals.⁶⁸

3.1.1. Nanoporous carriers. Common porous materials include porous metal oxides, mesoporous silicates, porous carbons, and porous polymers.⁶³ According to their pore size, porous substance can be categorized into macroporous, mesoporous and microporous materials.⁶⁹ Mesoporous and

microporous materials act as adsorbents^{70,71} or scaffolds for loading chromophores when utilized in metal ion detection. This improves recognition of the target toxic metals and enhance the generated signal. The large surface area of these materials provides more active sites for metal adsorption. The powerful and rapid response toward metal ions can be achieved by adjusting their surface area, and the pore diameter, allowing various metal ions monitoring and a low detection limit. Mesoporous silica and metal-organic frameworks have been used to design optical chemosensors.^{72,73}

3.1.1.1. Mesoporous silica. The large surface area and stability of mesoporous silica nanomaterials enabled their utilization as carriers in the fields of sensing⁷⁴ and catalysis.⁷⁵ The soft and hard template methods were used to fabricate different structures and formation of mesoporous cavity. In the hard template approach, the rattle-type of silica nanoparticles was prepared with controllable morphology and structure. The calcination process is used for preparation of mesoporous silica as shown in Fig. 3. Therefore, the synthesis of MSN is conducted under relatively mild conditions (Fig. 3). The mesoporous nanomaterials are employed in optical chemosensors as carriers of chromophores for enhanced heavy metal recognition. To detect the selected heavy metal ions, the outer surface of MSN nanomaterials is decorated with the organic chromophore *via* physical or chemical interactions.

3.1.1.2. Metal-organic frameworks. Metal organic frameworks (MOFs) are promising hybrid porous materials, prepared by joining metal-oxygen clusters with organic linkers. MOFs consist of metal nodes linked with organic ligands *via* coordinate bond, and the ligands play a vital role in designing high specific surface areas and porous structure.⁷⁶ Generally, the metal nodes and linkers play a significant role in the structure of MOFs (Fig. 4). The organic linkers are secondary building units (as rods) whereas the metal centers act as junctions of MOF constructions. To build up MOF structures, changing the metal centers and selecting a suitable linker are considered the main factors in designing the framework topology. The superior porosity with significant large pores over volume properties are tailored by broadened MOF's topology (Fig. 5). The substantial



Fig. 2 Fabrication of optical chemosensors using (A) metal organic frameworks (MOFs) and (B) mesoporous silica (MSNs).



Fig. 3 Preparation of mesoporous silica as nanoporous carrier. Briefly, TEOS (tetraethoxysilane) is reacted with a cationic surfactant (e.g., CTAB) in water/acetone/diethyl ether solvent to form mesoporous silica nanospheres (MSNs). Filtration is then carried out followed by calcination at 550 °C.



MOF pore volume is dependent on the organic linker size and bulky metal clusters' network. Moreover, MOFs are used for immobilizing catalysts on conductive scaffolds with high surface area and pore size. Owing to their crystallinity and porosity, the MSNs or MOFs were used as the carrier in optical chemical sensors for detection of common cations.^{77,78} MOFs materials were used for other applications such as catalysis⁷⁹ and gas adsorption/storage.⁸⁰

3.1.1.3. Other nanoporous carriers. Several nanomaterials have been utilized as porous carriers because of their unique characteristics.⁸¹ Nanocrystalline TiO₂ films were employed for colorimetric naked-eye detection of mercury in aqueous solution.^{82,83} Chey *et al.* investigated indirect determination of Hg²⁺ using ZnO nanorods.⁸⁴ Furthermore, polymeric carriers play an important role in protecting photochromic characteristics from environmental degradation. The flat sheet cellulose acetate membrane was used as a substrate for loading dithizone chromophore for naked eye detection of Hg²⁺.⁸⁵ Paper-based chemosensors (PBCs) were recently developed for monitoring Co²⁺ and Cd²⁺ in cosmetic products by adsorbing the chromophore onto filter papers coated with mesoporous silica.⁶⁴

3.1.2. Probe immobilization. The immobilization of an organic probe onto a suitable porous material or polymer matrix, has a significant effect on the sensor monitoring features. The common approaches for immobilization of optical chemosensors include impregnation techniques, covalent bonding, and doping approach (Fig. 6).

3.1.2.1. Impregnation of existing matrices. Impregnation is a classical method for loading a chromophore on a porous carrier. In this approach, a thin support film of the carrier is

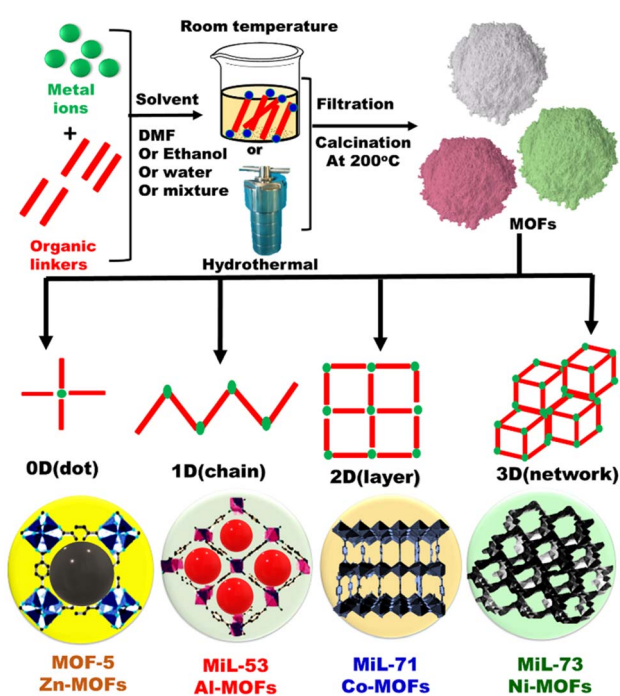


Fig. 4 General schematic representation for fabrication of metal organic frameworks (MOFs) with different dimensions.



Fig. 5 Preparation, properties and applications of metal organic frameworks.

dipped into a saturated solution of chromophore and the solvent is left to evaporate.^{86,87} The organic chromophore is loaded into the polymer matrix *via* chemisorption or electrostatic interactions. Although the impregnation technique is inexpensive, leaching of the chromophore (due to weak bonds with the carrier) hinders the large-scale utilization of this approach.

3.1.2.2. Covalent bonding to existing matrices. In this approach, the optical chromophore is chemically bonded to the surface of mesoporous or microporous materials *via* its functional groups. Alternatively, the chromophore may interact chemically with certain monomers to form a copolymer.^{88,89} Chemosensors prepared by covalent immobilization are highly stable and can be used multiple times. Disadvantages of chemosensors prepared by this method include low sensitivity and extended response time.

3.1.2.3. Doping. This is the most commonly used approach for immobilization of optical probes onto nanomaterials. Significantly, the selected chromophore is introduced to the porous nanomaterial solution during the preparation process.^{90–93} An optical sensor prepared by the doping method



Fig. 6 General schematic diagram of different immobilization approaches of organic probes on different carriers.



has high stability as compared to that prepared using the impregnation technique. Moreover, the response time is better than that observed with chemosensors prepared using the covalent bonding approach.

4. Detection of AD related heavy metals

Optical chemosensors can be divided according to the mechanism scheme into three main categories: carrier-based ion sensing, intrinsic metal ion sensors, and indicator-mediated ion sensing.⁷⁸

4.1. Mercury (Hg)

Kongasseri and co-workers reported the fabrication of sensor for the quantification of toxic Hg^{2+} ions through sol-gel process using two different block-polymer surfactants (PEO and F108) *via* doping method. The low limit of detection for probe anchored F108-MSM in sensing of mercury ions was 0.61 and 2.05 ppb; respectively (Fig. 7A). The sensor can be reused over 12 times for six months of storage.⁹⁴ Radwan *et al.*, used optical chemosensors *via* impregnation method of bis(4-(dimethylamino)phenyl) methanethione into Al-MOFs for sensing Hg^{2+} in water samples and skin whitening products.⁹⁵ The sensitivity and adsorption capacity of optical chemosensors for Hg^{2+} were 0.8 ppb and 1110 mg g^{-1} ; respectively (Fig. 7B). The Hg^{2+} sensor was used after multiple regeneration/reuse cycles (>9 cycles). Simple optical

sensor for monitoring and removal of Hg^{2+} from aqueous media using amino-functionalized MOF with ninhydrin was designed by Shahat and co-workers using covalent bonding approach.⁹⁶ They detected Hg^{2+} with a low limit of detection of ~ 0.494 ppb in water and the sensor can be for (≥ 6) cycles (Fig. 7C).

4.2. Cadmium (Cd)

Aluminosilica-based network platforms were used as carriers in designing optical sensors *via* direct impregnation of TMPyP moieties without any surface modification. The optical sensor was used for detection and removal of Cd^{2+} ions at low concentrations (10^{-10} mol dm^{-3}) for different analytical applications (Fig. 8A).⁶⁹ Shenashen *et al.*, used aluminosilica carrier to immobilize chromophore for Cd^{2+} ions detection using impregnation approach (Fig. 8B). This optical chemosensor was utilized for removal and visualization of some toxic metals such as Cd^{2+} at ($\sim 10^{-11}$ mol dm^{-3}) in water and a suspension of red blood cells (RBCs) and could be regenerated/reused for 6 cycles.⁹⁷ Shahat and co-workers developed an optical sensor based on Zr-MOFs (UiO-66) for detection, and removal of Cd^{2+} ions. The UiO-66 was used for impregnation of dithizone (Fig. 8C) without any coupling agent. The reported detection limit was 10^{-10} mol dm^{-3} and could be reused for 6 times.⁹⁸ Radwan *et al.*, designed optical chemosensors *via* using impregnation technique of the 1-(2-pyridylazo)-2-naphthol with the mesoporous cavities of nanospheres silica for visual



Fig. 7 (A) Schematic diagram for sensing Hg^{2+} ions using bis(diethylamino)-3oxospiro[isindoline-1,9'-xanthen]-2ylcarbamothioyl)-4-butylbenzamide (BOICB) probe.⁹⁴ (B) Schematic representation of fabrication of nanorod TAM optical chemosensors and interactions with Hg^{2+} ions under optimum conditions.⁹⁵ (C) Representative design of the Nin-NH-MIL-101(Al) sensor applied for purification of water polluted with $\text{Hg}(\text{II})$ ions and the reversible process by using 0.1 M thiourea solution (which can be repeated several times).⁹⁶ Reproduced with permission from ref. 94–96.

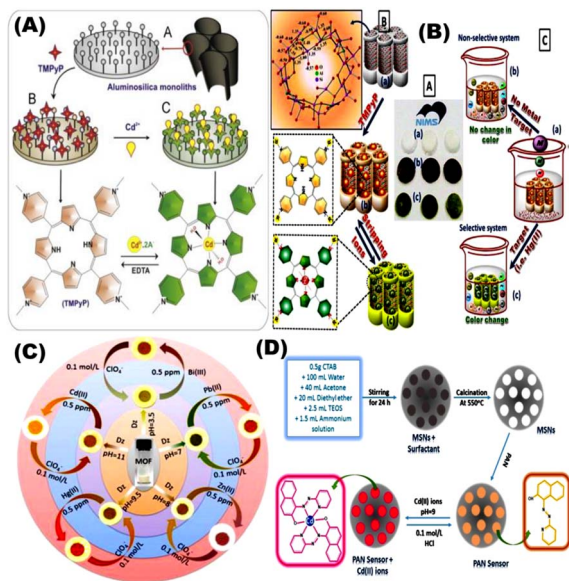


Fig. 8 (A) General schematic presentation of optical chemosensors based on aluminosilica network platforms *via* direct functionalization with δ -tetrakis(1-methylpyridinium-4-yl)porphine *p*-toluenesulfonate for $\text{Cd}(\text{II})$ ions detection.⁷⁶ (B) Chelating ligand immobilized meso-structures Ia 3d aluminosilica for visualization and removal of $\text{Cd}(\text{II})$.⁹⁷ (C) The Zr-based metal-organic frameworks (UiO-66) with its micropore geometry for the visual detection, determination and removal of ultra-trace of some toxic metal ions such as Cd^{2+} .⁹⁸ (D) General steps of fabricating Cd^{2+} ion optical chemosensors built on mesoporous nanosphere silica for naked-eye determination of ultra-traces of Cd^{2+} ions.⁹⁹ Reproduced with permission from ref. 69,97–99.





Fig. 9 (A) General representation of fluorescent probe prepared based on amino-functionalized metal-organic frameworks (MOF-5-NH₂) for the detection of Pb²⁺.¹⁰⁰ (B) Ratiometric fluorescent (RF) probe CDs/QDs@ZIF-8 by encapsulating carbon dots (CDs) and thioglycolic acid modified CdTe quantum dots (QDs) into porous metal-organic frameworks (MOFs) for detection of Pb²⁺.¹⁰¹ (C) Phosphorescent sensor to monitor Pb²⁺ using metal-organic framework-5.¹⁰² Reproduced with permission from ref. ^{100–102}.

detection of Cd²⁺ in water samples. Digital image analysis was applied to determine the Cd²⁺ concentration in well water samples with a low detection limit of 10^{−9} mol L^{−1}. The sensor could be stored for more than 8 months and reused for (*i.e.* ≥9) cycles.⁹⁹

4.3. Lead (Pb)

Xuanxuan and coworkers prepared fluorescent probe based on amino-functionalized MOFs (MOF-5-NH₂) using covalent bonding approach for sensing of Pb²⁺ using a single step

synthesis (Fig. 9A). The Pb²⁺ coordinated with the amino groups on the surface of the MOF-5-NH₂ thus allowing for fluorescence quenching with a low limit of detection of 0.25 μmol L^{−1}.¹⁰⁰ Kuiyu Yi and Lei Zhang designed fluorescence probe by encapsulating thioglycolic acid modified CdTe quantum dots (QDs) and carbon dots (CDs) into porous (MOFs) for detection of Pb²⁺ using doping method in biological samples (Fig. 9B).¹⁰¹ Shifen Xua and coworkers developed Pb²⁺ phosphorescent chemosensors using MOF-5. The Pb²⁺ chemosensors showed a low detection limit of 2 nmol L^{−1} and linear range of 0.01–10 μmol L^{−1} (Fig. 9C). They prepared phosphorescent chemosensors in a polyethylene glycol film using impregnation method, which exhibit color change at 1.0 μmol/L^{−1} Pb²⁺ under 365 nm UV light.¹⁰²

4.4. Arsenic

Biswajit *et al.* reported a carboxylate-rich MOF for As(III) detection where a linear increase in the fluorescence intensity was observed for arsenic concentration in the range of 3.67–332 ng L^{−1}.¹⁰³ In another work, a MOF functionalized nanoconjugate material was prepared by Shahat *et al.* for selective sensing of As(V) and phosphate in the aqueous media. The detection limits of As(V) and phosphate were 0.15 μg L^{−1} and 0.13 μg L^{−1}, respectively. Detection was observed *via* change of the MOF color to blue, which was analyzed by UV-vis spectroscopic techniques.¹⁰⁴ Different chemosensors were utilized for detection of mercury, lead, cadmium, and arsenic were listed in Table 2.

5. Challenges in the field of optical sensors

Although qualitative results generated by optical chemosensors are useful to identify contaminated water sources, quantitative

Table 2 Chemosensors used for detection of mercury, cadmium, lead, and arsenic ions

| Metal | Chemosensors | Substrate | Probe mechanism | Detection limit (μM) | Ref. |
|-------|--|---------------|-----------------|----------------------|------|
| Hg | Probe anchored F108-MSM | MSNs | Absorbance | 0.003 | 94 |
| | Bis(4(dimethylamino)phenyl) methanethione into Al-mofs | MOFs | Absorbance | 0.0039 | 95 |
| | Amino-functionalized MOF with ninhydrin | MOFs | Absorbance | 0.0024 | 96 |
| Cd | Aluminosilica-based network platforms | Aluminosilica | Absorbance | 0.03 | 69 |
| | A porphyrinic chelating ligand | Aluminosilica | Absorbance | 0.03 | 97 |
| | Optical sensor based on Zr-mofs (uio-66) | MOFs | Absorbance | 0.18 | 98 |
| | 1-(2-Pyridylazo)-2-naphthol with the mesoporous silica | MSNs | Absorbance | 0.034 | 99 |
| Pb | Amino-functionalized MOFs (MOF-5-NH ₂) | MOFs | Fluorescence | 0.25 | 100 |
| | CdTe quantum dots (QDs) and carbon dots (CDs) into porous (MOFs) | MOFs | Fluorescence | 0.0235 | 101 |
| | Phosphorescent chemosensors using MOF-5 | MOFs | Phosphorescence | 0.02 | 102 |
| As | Carboxylate-rich MOF | MOFs | Fluorescence | 0.049 | 103 |
| | MOF functionalized nanoconjugate material | MOFs | Absorbance | 0.15 | 104 |



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