Review

Tuning photoactive metal–organic frameworks for luminescence and photocatalytic applications

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ABSTRACT

Metal-organic frameworks (MOFs) are a class of porous materials, constructed from organic and inorganic components. MOFs have been explored for a diverse range of applications due to their tunable structures, porosities, and properties. This review highlights examples of the applications of photoactive MOFs, with a focus on the effect of MOF components, such as organic linkers, inorganic units and framework guests, on the optical and electronic properties of the materials. Developments in utilising luminescent MOFs as chemical sensors and as light emitting materials are discussed, in addition to recent advances in designing MOF-based photocatalysts for water splitting, CO₂ reduction and organic reactions.

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1. Introduction

Metal-organic frameworks (MOFs), or related porous coordination polymers (PCPs) can be regarded as a class of porous crystalline materials, which self-assemble from organic linkers and individual metal ions or coordination cluster nodes.[1,2] The organic linkers are multideterminate species, which bridge metal ions or cluster moieties to form extended two- or three-dimensional structures. Early pioneering work demonstrated that through variation of the components used to construct MOFs, a wide range of structures were accessible.[3–9] Research into the control of the architecture of MOFs led to the development of reticular chemistry and related topological concepts.[10]

Reticular chemistry concepts are based on the realisation that a MOF can be reduced to the geometrical features of its subcomponents and categorised accordingly.[10] The inorganic node of the structure determines the relative orientation in which the organic linkers assemble. The organic linkers serve as geometrically defined connectors between the inorganic subunits. Both organic and inorganic components are often classified as secondary building units (SBUs), in analogy to zeolite topochemistry.[11,12] Reticular synthetic approaches take advantage of the specific geometries and chemical amiability of SBUs, producing extended network structures whose topologies relate to those of purely inorganic ‘default’ structures. A key principle that governs the synthesis of MOFs stems from the realisation that MOFs whose components possess the same geometrical features form isoreticular structures that adopt analogous topologies, or the same nets.[13]

As reticular chemistry and related synthetic concepts gained increasing importance, and their applications resulted in the discovery of prodigious numbers of new structures, universal nomenclatures for structure classification and identification were developed, for instance through collaborative efforts between Blatov, O’Keeffe and Proserpio.[14] The Reticular Chemistry Structure Resource (RCSR) database categorises the structures according to their topologies[15]; the RCSR symbols are composed of three lower case bold letters with abbreviations either based on materials with that topology (e.g. dia for diamond or pto for platinum oxide) or geometrical shapes (e.g. pcu for primitive cubic lattice or sq1 for square lattice, etc.).

In addition to their tunable structures and pore volumes,[16,17] MOFs and related metal–organic materials offer an advantage over other conventional inorganic porous materials, such as zeolites, as their properties can be tuned for specific applications by varying the nature of the linkers and the metal ions in the structure.[18–20] Additionally, the porosity of MOFs allows incorporation of various guest molecules into their voids, which can influence the properties of the materials.[21] The chemical and structural versatility of MOFs, as well as their potentially high surface areas and porosity, have facilitated their application as catalysts,[22–24] materials for gas storage[25] and separation,[26,27] as chemical sensors,[28,29] as photosensitisers for photodynamic therapy[30] and other applications.[31]

The ability to incorporate photosensitising ligands (e.g. organic chromophores, polyaromatic coordinating ligands, suitable coordination complexes, etc.) into MOFs has led to their development as light-harvesting materials.[22,32] Significant research activities have been carried out to investigate how the choice of the organic linker and inorganic node used in the construction of MOFs, as well as interactions with guest molecules, allow their photochemical properties to be controlled.[33] Hence, by systematic variation of the individual MOF components, the light absorption characteristics, as well as the luminescence output can be tuned towards specific wavelengths.[34] Additionally, MOFs can be tailored towards photocatalytic applications by incorporation of the appropriate components or functional groups.[35–37]

Herein, the design principles of photoactive MOFs are highlighted, in the context of two key aspects. A primary section discusses the application of MOFs as photoluminescent materials, for example, as light emitting materials with tunable emission characteristics, and as chemical sensors with luminescence responses. The second aspect explores the design of MOFs as photocatalysts for energy-conversion reactions such as water splitting, CO2 reduction or for light-driven organic reactions, such as degradation of organic pollutants. Particular attention is given to how the choice of the constitutional components of MOFs influences the photoactivity of these materials. This article is not intended to be a definitive comprehensive review of the current state-of-the-art within this fast developing field of research, however, it will explore some selected examples of recent advancements in areas which may provide inspiration for those new to the research field. Organic linkers of the individual MOFs that are discussed, and their abbreviations are shown in Fig. 1.

2. Photochemistry of MOFs

2.1. Absorption of light by MOFs

The design and synthesis of a photoactive MOF requires the incorporation of a light-harvesting unit into the structure. Typically, this is achieved by using an appropriate organic component in the MOF structure, though light-harvesting guests can also be incorporated into the voids of the porous framework.[38] In some rarer cases, direct excitation of metal ions or metal clusters is also possible, for example, in FeIII-based MOFs containing [Fe3+((3-O)7+)] clusters.[39] By varying the organic linker, MOFs can be designed to absorb light in specific regions of the UV–visible spectrum.[40]

Many MOFs utilise aromatic organic linkers, which absorb light in either the UV or visible region of the spectrum.[41,42] Excitation of these organic linkers leads to n–π* or π–π*–based transitions. The range of wavelengths in which these compounds absorb light can be varied by extending the conjugated aromatic system of the linker, or incorporating various functional groups on the backbone structure of the linker.[43,44] Alternatively, metalloligands can be employed as photosensitisers in MOFs. Of note are MOFs composed of metalloporphyrin ligands, which show great promise as photoactive materials, due to their ability to absorb visible light across a broad region of the spectrum. The photocatalytic properties of metalloporphyrin-based MOFs can be varied by changing the metal ion within the porphyrin cavity. For example, metallation of porphyrin linkers with high valent metal ions such as InIII and SnIV gives MOFs with oxidative photoexcited states that can facilitate organic reactions, for example, the Mannich reaction, aerobic amine coupling, and hydroxylation of arylboronic acids.[45] Thus, porphyrinic MOFs are being explored as promising and versatile photocatalytic materials.[46,47]

Furthermore, the use of polyarylidyl ligands that can facilitate ligand-centred, metal-to-ligand and ligand-to-metal–based transitions can be used in the generation of photosensitisers in MOFs. MOFs based on RuII or IrII photosensitisers, which are well known as excellent photo-cleavage agents for nucleic acids such as DNA,[48,49] have been widely reported in recent times.[50,51] RuII polyarylidyl-based photosensitisers offer advantages as linkers due to their ability to harvest visible light,[52] their long-lived excited states, and their ability to undergo photoinduced redox reactions.[53] Metalloligands employing earth-abundant metal ions have also been incorporated into MOF structures as photosensitisers, for example those based on CuI species.[54,55]
Fig. 1. A small selection of organic linkers used in the construction of photoactive MOFs, and corresponding abbreviations as they appear in this article.
The diversity of ligands that can be used in the construction of MOFs can allow for further tuning of the optical band gaps of these materials. For example, by functionalisation of the ligand used in a MOF denoted as MIL-125 (MIL = Matériaux de l’Institut Lavoisier), the optical band gap of this material could be varied. MIL-125 consists of 1,4-benzenedicarboxylate (BDC 2-) linkers that bridge octanuclear cyclic Ti-oxo clusters. Walsh and co-workers reported that the introduction of amine functional groups onto the BDC 2- linker of MIL-125 led to a shift of the absorption onset of these MOFs from the UV region to the visible region of the electromagnetic spectrum. Furthermore, functional groups which impart weaker electron donating effects than amines revealed a reduced influence on the band gap, with smaller shifts observed for -Cl, –CH3, and –OH substituents.

2.2. Luminescence processes of MOFs

Luminescence is defined as emission of light from a substance, which occurs following absorption of radiative energy, either directly or via sensitisation processes involving energy or electron transfer processes.[57] Two categories of luminescence exist, fluorescence and phosphorescence. Fluorescence occurs without a change in spin, when light is emitted from singlet excited states and fluorescence lifetimes are short, in the region of $10^{-12}$ to $10^{-6}$ s.[58] In contrast, phosphorescence occurs when spin-forbidden transitions occur resulting in the emission of a photon, for example, from triplet excited states to singlet ground-states. Phosphorescence lifetimes are longer than those observed for fluorescence processes, with typical values varying between $10^{-6}$ and $10^{5}$ s.[58] While not common for organic ligands (except at low temperatures), phosphorescence can be facilitated through intersystem crossing by the so-called heavy atom effect that is characteristic for many d- and f-block metal complexes (e.g. RuII polypyridyl complexes which normally emit from ‘MLCT states).

Generally, luminescence occurs following absorption of radiation of a specific wavelength, commonly, X-ray, UV or visible light, and emission of light at a different wavelength. The emitted light is usually lower in energy than the absorbed light, and the difference in energy between the maximum of the absorbed light and the maximum of the emitted light is known as the Stokes shift. Alternatively, upconversion may occur, a phenomenon in which absorption of two or more photons results in the emission of one photon of higher energy.[59] In this case, the energy difference is quantified by the anti-Stokes shift.

Due to the hybrid nature of MOF structures, luminescence in MOFs can arise from multiple different sources, as highlighted in Fig. 2. These include,

- Ligand-centred emission
- Ligand-to-ligand charge transfer (LLCT)
- Ligand-to-metal charge transfer (LMCT)
- Metal-to-ligand charge transfer (MLCT)
- Metal-to-metal charge transfer (MMCT)
- Metal-centred emission
- Interactions with guest molecules.

Combinations of more than one of these effects can also be observed in luminescent MOFs.

Linkers in MOFs are constrained in ordered positions and as a result, the photochemical properties of the linkers differ from those of the free ligand in solution. In the rigid environment of MOFs, non-radiative processes from the linker excited state are less efficient, leading to enhancement of the linker fluorescence.[61–63] Ligand-centred emission is commonly observed in MOFs based on d10 metal ions such as ZnII and CdII systems.[64] Due to their closed shell electron configuration, d-d transitions cannot occur, and the metal ions cannot be readily oxidised or reduced, leading to ligand-centred emission characteristics.

Luminescence can also occur via LMCT and MLCT interactions in MOFs. Charge-transfer luminescence occurs due to a transition from the charge-transfer excited state to the ground state. LMCT excited states occur via transfer of electrons from an orbital centred on a linker, to an orbital of a metal ion. The opposite effect is facilitated by MLCT, which involves electronic transitions from

![Fig. 2. Schematic representation of the absorption and emission processes in photoactive MOFs, showing examples of photoactive organic linkers and inorganic nodes are represented by hexagons. Polyoxometalate (POM) structure produced from Ref. [60].](image-url)
metal orbitals to orbitals of the linkers. MLCT is commonly observed in MOFs containing metal ions in low oxidation states, that can readily be oxidised further.

Metal-centred emissions are typically observed in lanthanide-based MOFs (Ln-MOFs). In these systems the shielding of the 4f orbitals by the 5p66s2 shells results in characteristic narrow-line emission, predominantly in the visible and near-infrared regions of the electromagnetic spectrum. The f-f transitions are Laporte forbidden, hence, the absorption coefficients for these transitions are small, typically less than 3 M⁻¹ cm⁻¹. To excite lanthanide ions effectively, the antenna effect must be employed, in which a ligand coordinated to the LnIII ion acts as a light harvesting chromophore which sensitises the excited state of the lanthanide ion. Absorption of energy by the ligand results in spin-allowed excitation from the ground state to the singlet excited state S₁ (S = singlet). Intersystem crossing (ISC) can then occur from the ligand-centred S₁ excited state to the triplet excited state, T₁ (T = triplet). Energy can then be transferred from the long-lived ligand triplet excited state to the LnIII ion. Emission from the resulting LnIII excited state occurs spontaneously, giving metal-centred luminescence in the absence of back energy transfer to the excited state of the ligand. The latter may either reduce the efficiency of the emission process, or quench it entirely. The T₁ to LnIII transfer may be facilitated by good overlap between the linker and metal orbitals, involving a double electron transfer, in line with an exchange or Dexter mechanism. More predominate in coordination compounds is a Förster mechanism, whereby the dipole moments of the 4f orbitals couple the dipole moment of the T₁ state. Similarly, dipole–multipole transfers and charge-transfer states can play a role in the sensitisation of LnIII ions. In mixed-metal MOFs composed of transition metal-based linkers and LnIII nodes, sensitisation of the LnIII ions can occur via the 3MLCT excited states of the transition metal. Metal-centred emission following sensitisation is also observed in actinide-based MOFs.

A simplified diagram for the energy migration pathways applicable to Ln-based MOFs is shown in Fig. 3.

The porous structures of MOFs allow the possibility of introducing luminescent guest molecules into their pores. The crystalline nature of MOFs allows guests in the pores of the material to be characterised in detail. Luminescence can arise from these guest molecules from both the MOF and the guest molecule separately, or via interactions between these guest molecules and the framework structure. The interactions between the guest molecule and the MOF can occur via weak intermolecular interactions, dipole interactions, or through coordination bonds between the guest and open coordination sites on the framework metal ion.

2.3. Photocatalysis

Fossil fuels are the world’s primary energy source, accounting for over 80% of global energy consumption. Combustion of fossil fuels results in emission of greenhouse gases, and consequently, the increase of global temperatures. As emissions continue to rise, and fossil fuel reserves are depleted, the need for clean energy sources is increasingly urgent. Solar energy is a renewable and unlimited resource, and much research has focused on harnessing this energy to meet the world’s energy demands in a sustainable way. Designing materials that can use light to carry out reactions such as H₂O splitting or CO₂ reduction is vital to provide a sustainable method of producing energy.

Photoactive MOFs have been shown to be promising photocatalysts for energy conversion due to their tunable structures and properties. MOFs can behave as heterogeneous catalysts, and offer an advantage over molecular photocatalysts, as their solid-state nature allows facile separation of catalyst from product, thus lowering the risk of contaminating products with toxic metals used for catalysis. Heterogeneous catalysis also allows the catalyst to be recycled readily. Due to the crystalline nature of MOFs, the active sites are arranged in well-defined spatial sites, and the pores of MOFs can be tuned towards specific dimensions, which offers the potential for substrate selectivity. Furthermore, porous MOFs are often characterised by a high number of active sites per volume and high diffusion coefficients, which are attractive properties in catalytic materials.
To function as a photocatalyst, MOFs are required to efficiently separate charges within their structures upon light absorption by a chromophore and promotion of an electron to a higher energy level. This electron can then migrate from the chromophore to a nearby electron acceptor moiety within the structure. The resulting negative charges (electrons) and positive charges (holes) can be used to drive chemical reactions (Fig. 4). Certain requirements are necessary for efficient photocatalysis, such as high molar absorption coefficients, excited state lifetimes that are long enough to allow catalytic conversion to compete with decay of the charge separated state, and finally, suitable redox potentials to drive the desired reactions.

3. Utilising MOF luminescence

3.1. Sensing

The ability to rapidly detect pollutants at low concentrations is vital to identify environmental risks and curtail pollution. The area of luminescent sensing focusing on small molecules and the receptor-spacer-fluorophore principles that govern the sensing process have recently been reviewed.[81] The underlying principles are transferable to MOFs, which offer some distinctive advantages over molecular sensors, associated with their intrinsic attributes including porosity and high surface areas. Luminescent MOFs can be used as sensors for a broad range of analytes, including gases,[82] explosive nitroaromatic compounds (NACs),[83,84] cations,[85,86] anions,[87,88] pesticides,[89] and other organic compounds.[90,91] The luminescence response from MOFs upon detection of analytes can result in luminescence quenching,[92] luminescence enhancing,[93,94] or a change in the colour of light emitted.[95,96] Nanoscale MOFs have even been reported to be capable of pH sensing within living cells.[97]

Several mechanisms for luminescence sensing of analytes have been reported in MOFs. These include linker-analyte ion interaction, collapse of the MOF structure in response to the presence of an analyte, cation exchange between the analyte metal ions and framework metal ions, and competitive absorption of excitation wavelength due to overlap of absorption spectra of the MOF and analyte.[98] The advantage of using MOFs that display sensing through non-destructive mechanisms, such as linker-ion interactions, is that the sensor materials can be readily recycled.[99]

3.1.1. Sensing of organic compounds

The first example of a MOF capable of sensing explosive compounds was reported in 2009.[100] Li and co-workers demonstrated that the luminescent MOF $[\text{Zn}_2(\text{BPDC})_2(\text{BPEE})]$ ($\text{BPDC}^{2-} = 4,4\text{-biphenyldicarboxylate, BPEE} = 1,2\text{-bipyridylethene}$) (Fig. 5a)) is capable of fast, sensitive and reversible detection of explosive compounds. The structure of $[\text{Zn}_2(\text{BPDC})_2(\text{BPEE})]$ features one-dimensional channels which are approximately rectangular in shape (Fig. 5b)). These channels contain DMF solvent molecules which can be removed to give a guest-free MOF. The luminescence quenching response of $[\text{Zn}_2(\text{BPDC})_2(\text{BPEE})]$ after solvent removal was tested for two analytes, 2,3-dimethyl-2,3-dinitrobutane (DMNB), a volatile organic compound (VOC) used as a taggant for explosives and 2,4-dinitrotoluene (DNT), a volatile impurity found in 2,4,6trinitrotoluene. Thin layers of $[\text{Zn}_2(\text{BPDC})_2(\text{BPEE})]$ could be rapidly recovered after sensing, by heating the layers at 150 °C for one minute. The quenching...
An example of the use of an electrodeposited luminescent MOF was reported by Yang and co-workers, using the MOF $[\text{Eu}_{4}(\text{NDC})_{6-}\text{(H}_{2}\text{O})_{3}]\text{-3H}_{2}\text{O}$ (Eu-NDC; NDC$^{2-}$ = naphthalene-2,6-dicarboxylate). [105] Eu-NDC was first reported by Jin and co-workers in 2006. [106] The structure of Eu-NDC comprises channels with a compressed honeycomb-like shape, which run parallel to the crystallographic a-axis (Fig. 6a)).

Yang and co-workers reported the synthesis of Eu-NDC by electrochemical methods on the surface of fluorine-doped tin oxide (FTO) in 20 s.[105] Eu-NDC showed metal-centred luminescence under UV light irradiation ($\lambda_{ex} = 355$ nm). In the response the presence of picric acid dissolved in water samples, the MOF displayed luminescence quenching, with a detection limit of 0.67 $\mu$M. Furthermore, the MOF thin film could be washed and reused 5 times with no significant decrease in luminescence quenching (Fig. 6b)).

3.1.2. Sensing of metal ions

Many metal ions are toxic to human, plant and animal life, and as a result, the development of stable, reusable materials, which can rapidly detect the presence of metal ions at low concentration is desirable. Metal ions such as Li$^{+}$, Cr$^{3+}$, Hg$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ are dangerous to the environment, livestock and human health. Other ions are biologically essential, such as Cu$^{2+}$, Zn$^{2+}$, or Fe$^{3+}$, but are harmful at higher concentrations. Luminescent MOFs have been reported to function as effective sensors for a wide range of metal ions. In some cases, selective sensing of specific metal ions over other analytes is possible.[107] Selective sensing of ions has also been accomplished, in fact, MOFs have been reported to be capable of discriminating between Fe$^{3+}$ and Fe$^{2+}$ ions.[108]

As previously mentioned, a common mechanism for luminescence sensing of metal ions by MOFs is through interactions between the analyte metal ions and the organic linker of the MOF structure. This interaction can lead to quenching or enhancement of the MOF luminescence, or a shift in the wavelength at which the MOF emits light. In some rarer cases, the luminescence response can even be observed by the naked eye.[109,110] One approach which can increase the ability of MOFs to sense metal cations involves the functionalisation of organic linkers, for example, through introduction of functional groups containing Lewis-basic N, O or S atoms.

Nitrogen- and sulfur-containing linkers have been reported as promising linkers for selective detection of Hg$^{2+}$ ions, which is desirable due to the toxicity of these ions, and their potential for bioaccumulation. One example was reported by Wang and co-workers.[111] Reaction of Cd(NO$_3$)$_2$$\cdot$6H$_2$O and the organic ligand, 4,4',4'-s-triazine-1,3,5-triyltri-p-aminobenzoate (TATAB$^+$), gave a porous, luminescent MOF (Cd-TATAB) (Fig. 7). The organic linker features two kinds of Lewis-basic functional moieties, involving the central triazine ring and the surrounding amino functionalities (Fig. 7). Due to the high affinity of Hg$^{2+}$ ions for nitrogen donors, and the spatial orientation of the nitrogen atoms in TATAB$^+$, this MOF facilitates selective detection of Hg$^{2+}$ ions (Fig. 7c)), even in the presence of several other transition metal ions. In this case, the characteristic luminescence response arises from LMCT effects, which are influenced by Hg$^{2+}$-N interactions between the metal ions and the framework structure, leading to luminescence quenching and a red shift of the MOF-derived luminescence (Fig. 7d)).

In 2013, Su and co-workers reported a Zn-containing MOF, IFMC-28 (IFMC = Institute of Functional Materials Chemistry), using 3,4-dimethylthieno[2,3-b]thiophene-2,5-dicarboxylate (DMTD$^-$) as a linker (Fig. 8).[112] The Lewis-basic sulfur sites of the thienothiophene linker were identified as potential coordination sites for the selective chelation of metal ions. IFMC-28 showed selective adsorption of Cu$^{2+}$ ions over other metal ions, such as Pb$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Mn$^{2+}$, Mg$^{2+}$ and Cd$^{2+}$ ions (Fig. 8b)). This selective adsorption behaviour was not observed in experiments using the isoreticular MOFs, MOF-5 or IRMOF-3, as controls (Fig. 8c)). This selective adsorption behaviour could be applied to the use of IFMC-28 as an ion chromatographic column, which selectively favoured adsorption of Cu$^{2+}$ ions over Co$^{2+}$ ions, giving an efficient method of separating Co$^{2+}$ ions from Cu$^{2+}$ ions (inset, Fig. 8c)).

Many MOFs based on d$^{10}$ metal ions have been reported to display luminescence sensing as a result of interactions between functionalised ligands and analyte metal ions. For example, Zhang and co-workers reported two Cd- and Zn-based MOFs which can
Fig. 7. a) Ligand and inorganic SBU of Cd\textsuperscript{II}-based MOF, Cd-TATAB b) Structure of the MOF c) relative fluorescence intensity of Cd-TATAB (1) MOF in response to the presence of metal ions d) Changes in fluorescence spectra of Cd\textsuperscript{II}-MOF in response to increasing Hg\textsuperscript{II} concentration. Reproduced with permission from Ref. [111]. Copyright 2018, Elsevier B.V.

Fig. 8. a) Structure of IFMC-28 b) Metal ion absorption selectivity (graph) and Cu\textsuperscript{II} sorption over time when IFMC-28 was immersed in CuCl\textsubscript{2} solution (inset) c) Comparison of absorption of metal ions by IFMC-28, MOF-5 and IRMOF-3 and separation of Cu\textsuperscript{II} and Co\textsuperscript{II} ions by the MOF-based chromatography column (inset). Reproduced with permission from Ref. [112]. Copyright, Royal Society of Chemistry, 2013.
efficiently sense a range of transition metal ions.[113] These MOFs incorporate the ligand benzo-(1,2;4,5)-bis thiophene-2-carboxy late) (BBTC), and two different ancillary ligands. Both MOFs display luminescence quenching effects in response to Hg, Cu and Cr ions. These ions can be detected selectively by the MOFs from aqueous solutions containing other analytes. Luminescence quenching was also observed in response to the presence of the organic molecule salicylaldehyde in ethanol solution. Furthermore, in the case of Cr, Hg and salicylaldehyde, the sensing behaviour could be reproduced after washing the MOFs, demonstrating facile recyclablity of the system.

The detection of toxic anions in wastewater is important to prevent environmental contamination, and MOFs have been reported that can detect harmful pollutants such as CrO and CrO. [88,114] These ions present a serious risk to human health, causing DNA damage and cancer.[115] Li and co-workers have reported the synthesis of a luminescent 2r-based MOF, BUT-39 (BUT = Beijing University of Technology) which contains a tritopic imidazole ligand.[116] The luminescence in the MOF arises from ligand-centred emission. BUT-39 could selectively detect Hg and Fe ions through luminescence quenching effects. In terms of anion sensing, BUT-39 showed a selective sensing ability towards CrO, as the MOF luminescence was quenched by 99% in response to this anion. As this MOF luminescence response, the MOF also facilitated rapid removal of CrO from water. This dual potential of sensing and absorbing harmful ions from aqueous solutions demonstrates some of the advantages of utilising porous, luminescent MOFs as sensor materials.

3.2. MOFs for tunable light emitting devices

The emission of MOFs can be tuned using several different methods, including by linker variation, incorporation of dopant metal ions into the SBU of MOFs,[117,118] and absorption of guests which alter the luminescence properties of the MOFs.[119]

A strategy that has been effective in designing MOFs that are characterised by tunable light emission involves the synthesis of Ln-MOFs using multiple different lanthanide ions, to give mixed-lanthanide MOFs.[120,121] Every Ln ion, except La and Lu, is photoluminescent. This luminescence can be observed in the UV region (Gd), in the visible region (Pr, Sm, Eu, Tb, Dy, Ho, Tm) or in the near-infrared (NIR) region (Pr, Nd, Ho, Er, Tm, Yb).[67] These ions can be categorised as triplet state emitters whereby the emission is often referred to as ‘metal-centred’ or as ‘lanthanide delayed luminescence’; as crystal field effects are minimal and the emission generally arises from the deactivation of the lanthanide’s excited state. Due to their visible, ‘bright’ luminescence (which is due to their long-lifetimes in the millisecond time range, which overcomes autofluorescence from other shorter lived emitters and from light scattering), Eu (red emission) and Tb (green emission) ions in particular have been studied with great interest. Further, the use of most conventional and commercially available spectrometers allows for their emission to be recorded without the need of special detectors (as is the case for some of the NIR emitting ions). However, a drawback to the use of the lanthanides is that their excited states can easily be quenched by O–H oscillators of coordinating solvent molecules, particularly water and alcohols, as their narrow energy gaps can be quenched. The often observed on and off emission characteristics associated with binding or displacement of solvent molecules is often exploited in functional materials including MOFs.[122]

In some cases it is possible to dope different lanthanide ions into a MOF without changing the framework structure.[123] Facile synthesis of mixed-lanthanide MOFs with varying ratios of lanthanide ions can be achieved by controlling the stoichiometry of the reactant lanthanide ions during synthesis.[124–126] In mixed-lanthanide MOFs, multiple luminescence emission bands are observed from the different lanthanide ions in the structure, allowing modulation of overall emission colour.[127–130] Thus, strategic combination of lanthanide ions that emit light in different regions of the visible spectrum allows the luminescence output of the MOFs to be specifically tuned, depending on the desired application; particularly significant work has been dedicated to the use of lanthanide-based MOFs or related soft materials as white light emitters.[131–133]

A vast majority of known luminescent materials only show emission in one part of the visible region of the electromagnetic spectrum. Su and co-workers reported a series of isostructural mixed-lanthanide MOFs, which can be tuned towards a range of emission colours.[134] The MOFs in this series have the general formula [LnL] (TTP)H2O[Cl-solvent] (TTP = 1,1’-2,4,6-trimethylbenzene-1,3,5-triyl)tris(methylene)tris(pyridine-4(1H)-one)). Mixed-metal MOFs were synthesised using three combinations of two different ions; Eu and Tb, Eu and Gd, Gd and Tb ions. The structure of the MOF consists of seven-coordinate Ln ions, with pentagonal-bipyramidal geometry. Each Ln is coordinated by six oxygen atoms from six different TTP ligands and one water molecule. The MOF forms one-dimensional chains with channels within (Fig. 9a)).

The TTP ligand behaves as an antenna for photosensitisation of the Eu (red emission) and Tb (green emission) ions in the MOF (Fig. 9b)). The presence of methylene groups linking the pyridine groups to the core benzene rings allows each pyridine group to function as an independent sensitising antenna. Coordination of a pyridine group to Gd, which is non-emissive in the visible region, results in ligand-centred blue emission from the pyridine group. Changing the ratios of the lanthanide ions in the structure allowed the colour of the MOF luminescence to be varied across the RGB triangle.

Materials that exhibit white light emission are desirable due to their applications in displays and solid-state lighting.[135,136] Often, sources of white light are achieved by combining light sources, however this has drawbacks due to high costs and variations in colour.[137] Therefore the design of materials which can emit white light is a current topic of much research in the field of luminescent materials.[138]

In multicomponent MOFs, which contain more than one type of linker molecule, the emission of the MOF can be tuned by variation of each of the linkers in the structure independently, affording great control over the luminescence output of the material. For example, Telfer and co-workers have reported a multicomponent MOF controlled from three structurally different linkers, and demonstrated that the luminescence properties of this MOF can be controlled both by linker modification and guest binding (Fig. 10). [139] The constitutional composition of this MOF, abbreviated as MUF-77 (MUF; Massey University Framework) is given by the formula [ZnO(xhttξ2(BPDC)ξ2(BDC)ξ2)ξ2] (ξ = 5,5,10,10,15,15-hexaalkyl-10,15-dihydro-5H-diindenol[2,1-a,2’-c]fluorene-2,7,12-tricarboxylic acid (alkyl = methyl, butyl, hexyl or octyl)), BPDC, BDC, linker moiety resulted in yellow emission from the MOF, while addition of a –NH2 functional group to the BDC linker gave blue fluorescence. Combining the guanidine functionalised BPDC and the amine functionalised BDC group gave a white light emitting MOF. Additionally, the luminescence of MUF-77 could be tuned by interactions with guest molecules in the framework. In response to the presence of nitrobenzene, which interacts with the MOF through hydrogen bonding, the emission of the MOF was quenched. Interestingly, this quenching effect was stronger for the yellow emission band of the MOF, causing the luminescence output of the MOF to shift to a blue colour.
As demonstrated by some previously mentioned examples, the inclusion of guest molecules in MOFs also provides a method of tuning their photochemistry. The porosity of MOFs allows for incorporation of guest molecules which can influence the luminescence output of the material. For example, Qian and co-workers have reported that encapsulation of dye molecules into the structure of MOFs gives a method of modulating the colour of the luminescence output of the material. Two cationic dyes, acriflavine (AF), which emits green light, and 4-(p-dimethylamino)tyryl-1-methylpyridinium (DSM), which emits red light, were encapsulated in the anionic framework ZJU-28 (ZJU = Zhejiang University). ZJU-28 is an anionic MOF, with the formula $(\text{Me}_2\text{NH}_2)_3[\text{In}_3(\text{BTB})_4] \cdot 12\text{DMF}/\text{C}_2\text{H}_2\text{O}$ (BTB$^3$ = 4,4'$\text{O}$,4',4'-benzene-1,3,5-triyl-tribenzoate).[141] Prior to encapsulation of dyes, ZJU-28 emits blue light upon excitation with UV light ($\lambda = 365$ nm). Incorporation of the DSM dye into the structure of ZJU-28 gives tunable light emission, with blue emission observed at low dye concentration, and purple emission at high dye concentration.[140] A similar effect is observed when AF is encapsulated into the MOF, with green emission observed at high AF concentration. Encapsulation of the two dyes, AF and DSM, into ZJU-28, gives a mixed-dye exchanged MOF which emits white light. The potential of this material in white light emitting devices was also demonstrated by coating a UV-LED (LED = light emitting diode) with the mixed-dye-encapsulated MOF, resulting in warm white light emission from the MOF-coated LED.

Recently, MOFs have been reported for their application as organic light emitting diodes (OLEDs). OLEDs and LEDs are devices which generate light in response to an electric current. LEDs are typically constructed from semiconductor materials such as GaN or AlGaN, with the colour of light emitted depending on the band gap of the material. The emissive components of OLEDs are films of organic compounds or polymers. Compared to LEDs, which are typically rigid systems, OLEDs can possess increased flexibility, which, in principle, allows for displays that can be bent and rolled up.[142] Furthermore, OLEDs can be designed to be transparent materials.[143]

In 2018, Douhal and co-workers reported OLEDs based on a Zr-based MOF, Zr-NDC.[144] The structure of Zr-NDC is composed of $[\text{Zr}_6(\mu_4-O)_6(\mu_3-OH)_4(\mu_3-COO)]_2$ SBUs, which are 12-fold connected by the NDC$^{2-}$ organic linkers. This MOF displays electroluminescence, a property which is relatively rare in MOFs. Incorporation of dye molecules as guests into the MOF pores can effectively tune the optoelectronic properties of this material. Two different dye molecules were encapsulated into the MOF pores, Coumarin 153 (C153) and 4-(dicyanomethylene-2-methyl-6-(4-dimethylaminostyril)-4H-pyran (DCM). In the MOFs with encapsulated dyes, C153@Zr-NDC and DCM@Zr-NDC, two different emission bands are observed in the photoluminescence spectra, blue luminescence originating from the Zr-NDC MOF, and red luminescence from the encapsulated dye molecules. The photoluminescence bands of both dyes are shifted in the MOF environment compared to the pure
dyes in the solid state, indicating that interaction occurs between the MOF and the dyes in their pores.

To investigate the electroluminescence of Zr-NDC and the dye-encapsulated analogues, Douhal and co-workers designed light emitting devices with the MOF as a light emitting layer in a polymer matrix. The MOF displayed electroluminescence that could be modified by dye encapsulation. The dye encapsulated MOFs did not show a change in colour of electroluminescence, however, the electroluminescence intensity was increased in C153@Zr-NDC and DCM@Zr-NDC.

4. MOFs as photocatalysts

In view of sociologically important sustainable energy-related applications, MOF-based research activities can be directed towards artificial photosynthetic systems. Artificial photosynthetic systems that convert light into chemical energy, producing molecular O₂ and H₂, provide arguably the most attractive approach to green and renewable energy technologies. Photosynthesis is the process by which plants, algae and some bacteria use light energy to split water, and use the electrons and protons produced for the reduction of CO₂ to produce sugars. The process stores energy in chemical bonds. Insights into molecular details of these conversions can guide us towards employing solar energy to produce fuels, whereby the term ‘fuel’ in a broader sense can be thought of as a reduced molecule that can be oxidised, to produce desired compounds or energy as required. The replication in any artificial photosynthetic analogue is scientifically highly challenging but can be rendered more manageable when the overall process is separated into distinct sequential, partial processes: a) light harvesting, b) charge separation, c) reaction involving the positive cation.

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Fig. 10. Synthesis of luminescent MUF-77 nanocrystals and their luminescence output colours (R = methyl, butyl, hexyl or octyl groups). Reproduced with permission from Ref. [139]. Copyright 2018, American Chemical Society.
'hole' at the catalytic centre to oxidise a suitable electron donor molecule (water or other donor molecules) and d) reactions involving the mobilised electrons to produce a desired compound via the reductive process. Thus, by conceptualizing 'artificial photosynthesis' into these modular processes, catalytic oxidative and reductive processes may be developed and combined to give a highly efficient, optimised overall redox system.

The influence of the inorganic SBUs on the optoelectronic properties of MOFs was recently exemplified using five isostructural 2D MOFs which incorporate a Cu metallo-linker, \([\text{Cu}^2(\text{H}_2\text{2,2'-DMBP})_2]\) PF₆ \((\text{H}_2\text{4,4'-DMBP} = 6,6'-\text{dimethyl}-2,2'-\text{bipyridine}-4,4'-\text{dicarboxylic acid})\) (Fig. 11).[145] The MOFs, \([\text{Cu}(\text{H}(1-x)^2,2'-\text{DMBP})_2\text{M}_{0.5})\] \([\text{M}(\text{OH}2)_4]^x\) (M = Mn II (x = 0.47), Co II (x = 0.38), Cu II (x = 0.14), Zn II (x = 0.25), or Cd II (x = 0.32)), feature mixed mono- and dinuclear SBUs (Fig. 11a)). The compounds exhibit broad absorption in the visible region (Fig. 11c)) and emission centred at 728 nm. Compared to the parent photosensitisers, the MOFs' rigidity enhances intersystem crossing from the singlet to the triplet state and enables higher radiative decay rates, which depend on the nuclearity of the SBU and O–H oscillations of coordinated water molecules. Quantum yields depend on the chemical nature of the SBU, and are up to six times higher for the Zn II-MOF than for \([\text{Cu}^2(\text{H}_2\text{2,2'-DMBP})_2]\) PF₆. The shortest triplet excited state lifetimes are observed for the Cu II- and Co II- systems, as the excited states are quenched by rapid electron transfers to the SBU (Fig. 11d)). This series of MOFs demonstrates the potential for tuning photochemical properties by variation of the nature of the metal ions within the inorganic SBUs.

4.1. CO₂ reduction

Due to rising levels of atmospheric CO₂ from fossil fuel combustion, and the need to curb the associated rise in global temperatures, research into technologies that can capture CO₂ and convert it to value-added products is a source of high scientific and societal interest. Fixation of CO₂ to form valuable products such as CO and methanol has the potential to replace or alter current methods of synthesising these products, which use conventional fossil fuels as a feedstock.[146,147] However, the thermodynamic energy barriers associated with the conversion of CO₂ currently present a major challenge in implementing these new sustainable and cost-effective technologies.

MOFs have been explored as materials that can catalyse the reduction of CO₂ using visible light as an energy source.[148,149] Early catalysts for CO₂ reduction involved various metals or metal oxides such as TiO₂,[150] followed by the development of molecular homogenous catalysts.[151] However, the use of heterogenous photocatalysts for CO₂ reduction offers several advantages over homogenous catalysts.

The advantages of MOFs as heterogenous catalysts arise from their intrinsic properties and their ordered and well-defined nature, whereby associated reticular synthesis concepts offer some degree of synthetic control during assembly of the materials. This approach may allow the preparation of materials in which the components for photocatalysis, for example the photosensitiser, catalyst and sacrificial electron donor, can be oriented in an ordered and well-defined manner, thus optimising electron trans-
fer to the active site. The dimensions of the components determine the porosity and diffusion characteristics in the materials. Catalytic transformations may occur in confined spaces of molecular-sized cavities, involving structural intermediates and moieties that may relate to those of molecular catalysts, or which may not be attainable in condensed liquid phases. Hence, MOFs may provide synthetic avenues to bio-inspired materials that replicate some of the key features of enzymatic catalysts.

The development of photocatalytic MOFs for CO₂ reduction represents an area of intense research, and as a result, different generations of photoactive MOFs have emerged. First generation MOFs for photocatalytic CO₂ reduction employ the strategy of immobilising molecular photocatalysts in MOFs. First generation MOFs overcome some issues that arise when using homogenous catalysts, preventing dimerization of catalysts and the resulting loss of catalytic activity. Additionally, the environment within

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Fig. 12. Ir³⁺, Re³⁺ and Ru²⁺ metalloligands used by Lin and co-workers in the synthesis of doped UiO-67 frameworks. [153]

Fig. 13. Structures of MOFs formed upon reaction of a (Ru²⁺(phen)₃)-derived ligand with Eu³⁺ salts (left) [53] and Co³⁺ salts (right) [52].
MOFs offers advantages for photocatalytic reactions, such as high densities of catalytic active sites and good light penetration into their crystalline structure.[152]

Second generation photoactive MOFs are those which are capable of absorbing light in the visible region of the spectrum.[152] This characteristic is important in order to carry out photocatalysis efficiently using solar light as an energy source. Absorption of light by MOFs is typically tuned by variation of the organic linker in the system, emphasising the advantages of the tunable optical properties of MOFs. Third generation photocatalytic MOFs focus on electronic efficiency, by aiming to optimise the transfer of energy from the photosensitiser to the catalytically active site.[152] These materials should have charge separated states with lifetimes that are long enough to facilitate transfer of electrons to the CO₂ substrate.

In 2011, Lin and co-workers reported the first example of MOFs that could perform as heterogenous catalysts for H₂O oxidation, photocatalytic CO₂ reduction and light-driven organic reactions.[153] A series of stable, porous heterogenous catalysts were prepared by incorporating various catalytically active complexes as metalloligands into the UiO-67[154] (UiO = Universitetet i Oslo) framework.[2zrO₆(OH)₄(BPDC)₆] (Fig. 12). Varying the molecular dyes used as metalloligands changed the catalytic behaviour of the MOF. For example, using [ReCO₂(bpydc)Cl] (bpydc = 2,2'-bipyridine-5,5'-dicarboxylic acid) as a metalloligand enabled the MOF to perform as a heterogeneous photocatalyst for reduction of CO₂. A turnover number (TON) of 10.9 was recorded for the MOF, which was also employed for the formation of a Co II-based MOF that displayed high CO₂ adsorption capacities associated with the bifunctional phenanthroline-carboxylate ligand itself can be applied for the synthesis of photoluminescent Zn- and Mn-based MOFs displaying high CO₂ adsorption capacities associated with structural framework flexibility.[158]

Though RuII-based linkers have shown great potential as photosensitising ligands in photoactive MOFs, the development of catalysts using earth abundant metals is desirable. Fe-containing MOFs

In 2018, Zheng and co-workers reported the synthesis of a novel Eu-based MOF with a [Ru(phen)₃]⁻-derived (phen = phenylthionol) ligand, [Ru(4-(1H-imidazo[4,5-f][1,10]phenanthroline-2-yl)benzoate)₃] and dinuclear [Eu₂²⁺] SBUs (Fig. 13).[53] Europium was chosen due to the favourable reduction potential of Eu²⁺ for catalytic reduction reactions.[155,156] while the rational for use of the Ru(phen)₃-derived ligand was the redox activity and excited state lifetime of ruthenium polypyridine complexes.[157] Zheng and co-workers report the synthesis of a Ru²⁺/Eu³⁺ MOF, in which the carboxylate-bearing Ru²⁺-metalloligands bridge dinuclear [Eu₂²⁺] moieties, to give a MOF with large channels that penetrate the material (Fig. 13).[53] Each Eu³⁺ ion in the structure is nine-coordinate, and one μ₂-OH bridges the two ions in each dinuclear (Eu₂²⁺) unit. This MOF efficiently catalyses the reduction CO₂ to formate upon photolradiation with visible light (λₑₓ = 420–800 nm). Upon irradiation, the Ru²⁺ metalloligand is excited to its ³MLCT excited state, followed by PET from the ligand excited state to the [Eu²⁺-H₂O-Eu³⁺] unit. Transfer of two electrons results in the reduction of this unit to a photogenerated dinuclear [Eu²⁺-H₂O-Eu³⁺]²⁻ species, which reduces CO₂ to formate. The catalytic cycle is completed by reduction of the Ru³⁺ ion back to Ru²⁺ by a sacrificial electron donor. The same metalloligand was also employed for the formation of a Co⁰-based MOF that is characterised by hexagonal accessible helical one-dimensional channels (Fig. 13). Its structural characteristics facilitate relatively high CO₂ uptake capacities and selectivity over N₂. The photoactive porous material retains the photophysical properties of the Ru²⁺ nodes giving rise to emission centred at 620 nm and photoactivity associated with the ³MLCT states.[52] It is further noteworthy that the bifunctional phenanthroline-carboxylate ligand itself can be applied for the synthesis of photoluminescent Zn- and Mn-based MOFs displaying high CO₂ absorption capacities associated with structural framework flexibility.[158]
fulfil the criteria of containing earth abundant metals and have the added advantage that it is possible to use visible light to excite the Fe oxo-clusters of these MOFs directly. Excitation of the Fe oxo-clusters can lead to the transfer of an electron from the bridging $\text{O}^{2-}$ to $\text{Fe}^{III}$ ions, forming $\text{Fe}^{IV}$, which can facilitate the reduction of $\text{CO}_2$. A series of Fe-containing MOFs, MIL-101(Fe), MIL-53(Fe) and MIL-88B(Fe), have been reported as photocatalysts for reduction of gaseous $\text{CO}_2$ to formate in the presence of triethanolamine (TEOA) as a sacrificial electron donor.[159] Each of these MOFs contains the linker BDC$_2^-$, however the structures of the MOFs differ (Fig. 14). The structure of MIL-53(Fe) is composed of chains of vertex-sharing, hydroxo-bridged $\text{Fe}^{III}$ octahedra, which are connected by BDC$_2^-$ linkers. In contrast, both MIL-88B(Fe) and MIL-101(Fe) have oxo-centred ($\text{Fe}^{IV}_{x}(\text{H}_2\text{O})_y$) SBUs. In MIL-88B(Fe), BDC$_2^-$ linkers connect Fe$_2$O units to form a porous three-dimensional framework with microporous channels. However, the structure of MIL-101(Fe) contains mesoporous cages.

These structural differences lead to different catalytic activities for each material.[159] The best activity for photocatalytic reduction of $\text{CO}_2$ was recorded in MIL-101(Fe), due to the presence of a labile water molecule, which, when removed, leads to an unsaturated coordination site, allowing direct chemical adsorption of $\text{CO}_2$ onto the metal centre. Direct adsorption of $\text{CO}_2$ at the Fe sites was not observed for MIL-88B(Fe) or MIL-53(Fe). The difference in activity between these three MOFs shows the effect of the inorganic SBU structure on the photocatalytic activity of MOFs.

Further, modification of the organic linker can lead to enhancement of the catalytic activity for each of these Fe-containing MOFs. The catalytic activity of each of these three MOFs was enhanced by functionalisation of the BDC$_2^-$ linker by an amine group, to give three amino-substituted MOFs, NH$_2$MIL-101(Fe), NH$_2$MIL-53(Fe) and NH$_2$MIL-88B(Fe).[159] This improvement in catalytic activity was attributed to two factors. Firstly, the presence of a polar amino functionality increases the interaction with $\text{CO}_2$ molecules, leading to enhanced absorption capacity. Additionally, the amino group enables the adsorption of visible light, thus providing an additional pathway for the excitation of the Fe oxo-cluster through energy transfer from the excited ligand. The ability to tune the photocatalytic activity of MOFs by linker and node modification demonstrates the advantage MOFs can provide as molecularly-tunable catalytically active scaffolds.

Amine-functionalised Ti-based MOFs have also been reported as promising photocatalysts for $\text{CO}_2$ reduction. For example, Li and co-workers have reported that introduction of an amine group on to the BDC$_2^-$ ligand in a previously reported titanium-based MOF with octanuclear Ti units, MIL-125,[163] gave the isostructural MOF NH$_2$-MIL-125.[164] Under visible light irradiation, NH$_2$-MIL-125 can reduce $\text{CO}_2$ to formate. This photocatalytic activity was not observed in the unfunctionalised MIL-125 MOF under the same conditions.

MOFs have been explored as catalysts for selective reduction of $\text{CO}_2$ to $\text{CO}$. For example, Lu and co-workers have reported a MOF which utilises visible light to reduce $\text{CO}_2$ to syngas.[165] A mixture consisting primarily of $\text{CO}$ and $\text{H}_2$, which is used in a diverse range of industrial reactions for the synthesis of hydrocarbons, ammonia for fertiliser production and methanol.[166] Current industrial methods of producing syngas rely on fossil fuel sources. Hence, photocatalytic reduction of $\text{CO}_2$ offers a potentially sustainable method of producing syngas under mild conditions. Lu and co-workers designed a photoactive MOF, (Co/Ru)$_{2.4}$-Uio-67(bpydc). The photoactive MOF, (Co/Ru)$_{2.4}$-Uio-67(bpydc), was synthesised by functionalising the $\text{Zr}$-based Uio-67(bpydc) structure with a Ru$^{II}$-based photosensitiser, and a Co$^{II}$ single site catalyst (Fig. 15), whereby the Co:Ru ratio was controlled during the synthesis. In a saturated solution of $\text{CO}_2$ in CH$_3$CN and $\text{H}_2\text{O}$, containing TEOA as an electron donor, (Co/Ru)$_{2.4}$-Uio-67(bpydc) produced both $\text{CO}$ by reduction of $\text{CO}_2$, and $\text{H}_2$, by $\text{H}_2\text{O}$ reduction, when irradiated by visible light (Fig. 15). The syngas yield obtained was 13.600 $\mu$mol g$^{-1}$, which was 29.2 times higher than that obtained using the corresponding homogenous system. The relative composition of the $\text{CO}:\text{H}_2$ mixture was influenced by variation of the $\text{H}_2\text{O}$ content of the solvent system. Furthermore, systematically varying the Co:Ru ratio in the MOF allowed the CO: $\text{H}_2$ product ratio to be varied, thus rendering this MOF system a tunable photocatalyst for syngas production.

### 4.2. Photocatalytic water splitting

Using solar energy to carry out photocatalytic water splitting to produce $\text{H}_2$ and $\text{O}_2$ is a promising energy conversion and storage approach, providing a potentially sustainable alternative energy source to replace fossil fuels. The advantage that $\text{H}_2$ fuel sources possess over fossil fuels is that no emissions are generated from using $\text{H}_2$ as fuel.[167] Applications are severely hampered by the high production costs and lack of $\text{H}_2$ storage solutions for automotive and transport applications. Electrolysis of water is an energetically uphill process, and research is rapidly progressing to find catalysts for the two half reactions in $\text{H}_2\text{O}$ splitting, the oxygen evolution reaction (OER) (Reaction 1, Scheme 1) and the hydrogen evolution reaction (HER) (Reaction 2, Scheme 1).[168] A major challenge is developing catalysts for the highly endergonic OER reaction, as the potential required for each electron transferred at pH 0 is 1.23 eV versus NHE (NHE = normal hydrogen electrode).

To design efficient $\text{H}_2\text{O}$ oxidation catalysts, research activities may take inspiration from the oxygen-evolving complex (OEC) of photosystem II. From a molecular point of view, the 4-electron $\text{H}_2\text{O}$ oxidation half-equation, coupled to a transfer of 4 protons and the formation of an O-O bond, is one of the most challenging catalytic transformations, and insights into this process can guide the development of highly efficient oxidation catalysts. The complexity and energy demand of this reaction is illustrated by large...
overpotentials associated with the individual reaction steps. Thus, an energetically favoured catalysed pathway relies on concerted processes in which the substrate and catalyst adopt geometrically constrained conformations. Whilst artificial photosynthetic systems are severely hampered by a lack of active catalysts, nature uses a \([\text{Mn}_3\text{CaO}_5]\) oxo-cluster to oxidize water at efficiencies far exceeding those of any synthetic system. Recent X-ray, spectroscopic and computational studies resulted in new mechanistic insights into the oxidation process.[169–172] Active synthetic molecular oxidation catalysts that relate or mimic the naturally occurring process should be compatible with processes of the Kok cycle.[173] and enable multiple electron transfer (ET) or proton-coupled processes within a narrow potential range. In addition, they should be composed of abundant elements and should be amenable to structural modifications which allow them to interface with sensitisers.

MOFs have been explored as photocatalysts for \(\text{H}_2\) splitting due to their tunable photoactivity, large surface areas, favourable diffusion coefficients and high density of active sites per volume, as previously indicated.[31,174] The SBUs of MOFs can incorporate active sites for catalysis, including open metal sites, which have labile coordinating solvent molecules that can be exchanged for substrates during catalytic reactions.[175] The fundamental requirement of such labile coordination sites is exemplified in highly efficient biological or bio-inspired oxidation catalysts including dioxygenases, catalases or the oxygen-evolving complex of photosystem II. In addition, dynamic structures and multiple conformations that are typical for MOFs are widely recognised to be key characteristics, responsible for the performances of biocatalysts. MOFs may impart the principal advantages of heterogeneous catalysts compared to corresponding homogeneous phases, whereby enhanced stability or facile processability in photocatalytic systems can potentially lead to unique materials.

Cobalt-based MOFs have been reported as effective heterogeneous catalysts for light-driven water oxidation. In 2019, Chen and co-workers reported the synthesis of MAF-48 (MAF = metal-azolate framework), a cobalt-based MOF with the formula \([\text{Co}_{10}\text{[µ}_4\text{-OH}]\text{[BDT]_4(HTBDT)_2]}\) \((\text{HTBDT} = 1,4\text{-benzenedi}(1\text{-H}\text{-1,2,3-triazole})\)) which functions as a stable heterogeneous catalyst for water oxidation.[176] The structure of MAF-48 consists of octanuclear hydroxide-bridged \([\text{Co}_{10}\text{[µ}_4\text{-OH}]\text{SBUs}]\) linked by BDT linkers (Fig. 16). Each face of the octanuclear cobalt cluster features four coplanar Co\(\text{III}\) ions, coordinated to hydroxide ions which adopt \(\mu_4\)-bridging modes. In the presence of a photosensitisier, \([\text{Ru(bpy)}_3\text{]}\) \(\text{SO}_4\) and a sacrificial electron acceptor, \(\text{Na}_2\text{S}_2\text{O}_8\), MAF-48 demonstrates photodriven water oxidation when irradiated with visible light. A TOF of 3.05 s\(^{-1}\) and a TON of 1.2 \(\times\) 10\(^6\) were recorded, demonstrating the high catalytic activity of MAF-48. This study demonstrates the highest activity of any heterogeneous catalyst, except for photosystem II. This study demonstrates the influence of specific SBUs on the activity of MOFs as photocatalysts, as the high activity of MAF-48 was attributed to the structure of the octanuclear Co\(\text{III}\) hydroxo-cluster. The presence of four Co\(\text{III}\) ions that coordinate to a central \(\mu_4\)-OH\(^-\) hydroxo ligand leads to a stabilising effect on the reacting hydroxyl radical during the water oxidation cycle, thus enhancing the activity of the MOF.

Due to their ability to absorb visible light, porphyrins represent promising ligands for designing photocatalytic MOFs. For example, the MOF Ru-TBP (TBP\(^+\) = 5,10,15,20- tetra(p-benzoate)porphyrin) and its zinc-metallated analogue, Ru-TBP-Zn, have been shown to be effective at photochemical evolution of \(\text{H}_2\).[177] Ru-TBP-Zn was a better photocatalyst than Ru-TBP or TBP\(^+\) alone. The MOF is constructed from dinuclear \([\text{Ru}_{2}\text{]}\) paddlewheel SBUs linked by tetratopic porphyrin linkers. The mechanism for \(\text{H}_2\) evolution involved photochemical excitation of the TBP-Zn linker, and subsequent electron transfer to the \([\text{Ru}_{2}\text{]}\) SBU. The electrons transferred to the paddlewheel SBU consequently drive the proton reduction to generate \(\text{H}_2\).

While the reported MAF-48 system utilises \([\text{Ru(bpy)}_3\text{]}\)\(^2+\) as a photosensitisier,[176] various different photosensitisising ligands can be incorporated into the framework structures. For example, Lin and co-workers recently reported photocatalytic proton or \(\text{CO}_2\) reduction using a series of MOFs composed of photosensitising Cu\(^1\) metalloligands (Fig. 17).[54] Two different post-synthetic modification approaches were applied to obtain functional MOFs, which are iso-reticular to UiO-69 and comprise of inorganic \([\text{Zr}_{6}\text{[µ}_4\text{-O}_4]\text{[µ}_3\text{-OH}]\text{SBUs}]\) that are connected by \(\text{p-}

In the initial study,[55] both the Cu\(^1\)-based photosensitisier (Cu-PS) as well as the catalytically active site (Re\(^2\) or Co\(^3\) for \(\text{CO}_2\) or H\(^+\) reduction, respectively) were sequentially introduced at the PT linkages, yielding mPT-Cu/Re (Fig. 17b) and mPT-Cu/Co (Fig. 17c). In a follow-up study,[54] FeX@mPT-Cu (X = Br, Cl, OAc, BF\(_4\)) were obtained by sequential installement of the Cu-PS at the PT-links (Fig. 17f), followed by the introduction of catalytic centres at the inert SBUs through treatment with Fe\(^{11}\) salts (Fig. 17g). In all cases, the photocatalytic cycle is initiated by photoexcitation of Cu-PS to [Cu-PS]\(^+\), followed by a reductive quenching pathway, yielding [Cu-PS]\(^-\) and the oxidized sacrificial electron donor (1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole). Electron transfer from [Cu-PS]\(^-\) to the catalytic centre initiates the reductive transformation of the chosen substrate. The spatial proximity of the components in the MOF as well as the stabilising effect of the framework structure, enhances the catalytic activity in comparison to the corresponding homogeneous phases. When compared to the Cu-PS and Re\(^{1}\)- or Co\(^{3}\)-catalysts in solution, mPT-Cu/Re and mPT-Cu/Co exhibit enhanced catalytic activity by
almost two orders of magnitude, with respective CO₂ reduction reaction and HER TONs of 1328 and 18,700 (Fig. 17c and e)). The latter is exceeded further by FeX@Zr₆Cu, which display HER TONs of up to 33,700 for FeBF₄@Zr₆-Cu (Fig. 17h)). Further, it was found that the activity of FeX@mPT-Cu is dependent on the coordination strength of the charge-balancing X⁻ ion to the Fe²⁺ centre, with the weakest coordination resulting in the highest catalytic activity.

Encapsulation of catalytically active guests into the pores of MOFs can enhance their performance as photocatalysts for water splitting. For example, Kögerler and co-workers reported the encapsulation of two Co-based POMs into a MIL-100 (Fe) MOF.[178] an Fe³⁺ carboxylate MOF.[179] The two POMs encapsulated in the MOF, [Co⁴Co⁴III₇O₃₃(H₂O)₃]²⁻ (Co2) and [Co₄(PW⁹O₃₄)²⁻(H₂O)₂]¹₀⁻ (Co4) had previously been reported to display excellent activities as homogenous catalysts for water oxidation.[180,181] The water oxidation activities of the two composite materials Co2@MIL-100 (Fe) and Co4@MIL-100 (Fe) were studied at pH = 9 and 8 respectively, using Na₂S₂O₈ as a sacrificial electron donor and Ru(bpy)₃²⁺ as a photosensitiser (Fig. 18). Both POMs demonstrated higher catalytic activity when encapsulated into the MOF structure, compared to the POM alone, due to cooperative electrostatic interactions between the MOF and the POM guest. Furthermore, the activity of the catalysts did not significantly decrease when the catalyst was recycled, as the POMs did not leach from the host framework.

Lin and co-workers encapsulated a Wells-Dawson type POM, [P₂W₁₈O₆₄]⁶⁻, into the pores of a [Ru(bpy)₃]²⁺-derived UIO-type MOF.[182] Visible light irradiation leads to excitation of the Ru-based ligands to the ¹MLCT excited state, followed by intersystem crossing to the ³MLCT state. Subsequent multielectron transfer from the excited metallo-ligand to the encapsulated POMs...
Fig. 18. Schematic representation of photocatalytic water oxidation by composite materials Co2@MIL-100 (Fe) and Co4@MIL-100 (Fe).[178]

Fig. 19. Schematic representation of the mechanism of visible-light-driven proton reduction by the POM@UiO system. Reproduced with permission from Ref. [182]. Copyright 2015, American Chemical Society.

Fig. 20. a) Semiconductive MOFs Cu-X-4,4'-bpy as photocatalysts for H₂ evolution. b) Reflectance spectra and Tauc plot shown in the inset. c) Photocatalytic hydrogen evolution in aqueous TEDA (5% v/v, pH 11.5) under UV light irradiation. Reproduced with permission from Ref. [183]. Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
facilitates the latter to act as a proton reduction catalyst (Fig. 19). A series of POM@UiO materials were synthesised by variation of the quantity of POM in the reaction mixture, yielding highest activity at low POM loading. The materials were recycled thrice with only a minor loss of activity.

Incorporation of functional groups can also enhance the photocatalytic H2 evolution activity of MOFs. For example, introducing a methylthio group (-SCH3) onto the BDC2- linker of MIL-125 gave a MOF which was highly active for light driven H2 evolution.[35] Direct synthesis of MIL-125 with the methylthio-functionalised BDC2− (BDC-(SCH3)2−) linker was unsuccessful, and therefore the methylthio-functionalised MOF was synthesised by solvent-assisted ligand-exchange of BDC-(SCH3)2− into the structure of MIL-125. The resulting MOFs, 20%-MIL-125-(CH3)2, containing 20% BDC-(SCH3)2− and 50%-MIL-125-(CH3)2, containing BDC-(SCH3)2− showed visible light absorption and lower band gaps of 2.69 eV and 2.61 eV respectively, than that of MIL-125, which has a band gap of 3.8 eV. Additionally, in the presence of Pt as a co-catalyst, and TEOA as a sacrificial electron donor, the MOFs perform well as catalysts for H2 evolution from water. The highest H2 evolution activity was observed for Pt/20%-MIL-125-(SCH3)2 which had a H2 evolution rate of 3814.0 μmol g−1 h−1. The enhanced ability of Pt/20%-MIL-125-(SCH3)2 over Pt/50%-MIL-125-(SCH3)2 was attributed to the higher stability of Pt/20%-MIL-125-(SCH3)2.[35]

Recently, the groups of Liu and Du reported that MOFs [Cu2X2(4,4'-bpy)] (X = Cl, Br, I, 4,4'-bpy = 4,4'-bipyridine) denoted as Cu-X-4,4'-bpy,[183] whose basic structure had been known for 20 years prior,[184,185] are in fact semiconductors with narrow optical band gaps ranging from 1.85 eV for Cu-Cl-4,4'-bpy to 2.00 eV for Cu-4,4'-bpy (Fig. 20). In these systems, the [Cu2(μ2-X)2] units are linked by four 4,4'-bpy ligands, resulting in orthogonally interpenetrating layers of (3,6)-connected honeycomb nets. Importantly, the Cu-X-4,4'-bpy MOFs that self-assemble from inexpensive reagents, were found to be hydrogen evolution photocatalysts. The MOFs operate with visible light irradiation, without requiring any additional photosensitisers or co-catalysts. Particularly high activity and recyclability was demonstrated for Cu-I-4,4'-bpy using TEOA as a sacrificial electron donor.

4.3. Degradation of organic pollutants

Organic dyes, in addition to other pollutants, are the by-product of many industrial processes, and many are toxic to humans and to plant and animal life.[186,187] The ability to degrade organic pollutants into less toxic or even harmless compounds is essential for wastewater treatment technologies. MOFs can be designed to photocatalytically degrade organic dyes under various different conditions, including using samples of contaminated wastewater.[188]

In 2016, Zhang and co-workers reported that MIL-53(Fe) could be used as a heterogeneous catalyst containing earth-abundant metal ions for the photochemical degradation of the organic dye Acid Orange 7 (AO7) under visible light irradiation.[189] The catalytic activity originates from charge separated sites which form upon photoexcitation of the structure. However, the catalytic performance of MIL-53(Fe) was hindered by fast recombination of electron-hole pairs after excitation. This deficiency could be overcome by addition of an electron acceptor, sodium persulphate, which was necessary in order to prevent electron-hole recombination, thus enhancing the catalytic activity of the system. In the presence of persulphate, MIL53(Fe) could effectively decolourise a 0.05 mM aqueous solution of AO7 within 90 min of irradiation with a visible light LED (Fig. 21). No substantial difference in activity was recorded after five successive cycles of photocatalytic AO7 degradation, demonstrating that MIL-53(Fe) is a stable and reusable catalyst.

MOF thin films have also been reported as effective photocatalysts for photocatalytic waste treatment. A manganese-based MOF film composed of metalloporphyrin linkers was reported by Zhao and co-workers.[190] The MOF, which is constructed from the metalloporphyrin [5,10,15,20-tetra(4-carboxyphenyl)porphyrin][M nIII, 2,2'-dimethyl-4,4'-bipyridine (4,4'-DMBPP) and zinc acetate, was synthesised by layer-by-layer deposition onto a quartz glass substrate. The structure of the MOF consists of sheets of dinuclear (Zn2) SBUs connected by the tetratopic metalloporphyrin linker. The layers form parallel to the quartz substrate, and consecutive layers are linked by 4,4'-DMBP pillars. The MOF film was applied to the photocatalytic degradation of an aqueous solution of methylene blue with H2O2 under irradiation with visible light (400 – 700 nm). The MOF is stable, and can be recycled by washing and drying, and still performs as an effective catalyst after 5 catalytic cycles.

MOFs can also be employed in using visible light for photocatalytic degradation of antibiotics in aqueous solutions. Pollution of water systems by antibiotics can occur due to treatment of livestock with antibiotics.[191] As the incidence of antibiotic resistance increases,[192] the need to treat wastewater to remove antibiotics is vitally important. A europium-based MOF, with the formula [(CH3)3NH]2[Eu6(6H2O)6(ADBA)]15(DMF)15 (H2-ADBA = 4,4'-9-(10-anthracenediyl)dibenzoic acid), abbreviated as Eu-ADBA, has been reported to be effective in using visible light to catalyse photodegradation of the antibiotic tetracycline.[193] The linker in this MOF was chosen for the interesting optical attributes of its conjugated anthracene moiety. Eu-ADBA was capable of absorbing organic molecules into the MOF structure and using visible light to catalyse the degradation of two organic dyes, methylene blue and rhodamine B, and tetracycline in water.

Fig. 21. a) Changes in UV-vis spectrum during AO7 decolorization by the MIL-53(Fe)/persulfate/visible light process under the following reaction conditions: AO7 (0.05 mM); MIL-53(Fe) (0.6 g L−1); PS = persulfate (2.0 mM); initial pH 6.0. b) Mechanism proposed for photocatalytic AO7 degradation by MIL-53(Fe). Reproduced with permission from Ref.[189]. Copyright 2016, Elsevier B.V.
5. Conclusion

In recent years, MOFs have been explored as promising materials for a wide range of applications, some of which centre on their performance as photoactive materials. Here, characteristics of selected photoactive MOFs have been highlighted considering two broad areas, MOFs as luminescent materials, and photocatalytic MOFs.

The design principles of MOFs, that take advantage of self-assembly approaches and which are governed by the geometrical considerations of their sub-components, impart a degree of synthetic control which is somewhat rare within the area of synthetic materials science. The hybrid nature of the systems results in structural and physico-chemical amenability through both their organic and inorganic building units. Further, the porosity of MOFs often facilitates an extended interface enabling reversible interactions with analytes, substrates or other functionalising molecules which can locate in the cavities. The influence of these tenable features of MOFs are highlighted by the selected examples demonstrating how optical and electronic attributes can be influenced. Of particular note are emerging lanthanide-based MOFs or MOFs containing highly luminescent organic moieties. Through strategic selection of components, MOFs have been reported to be efficient and reusable sensors for a wide range of analytes.

The underlying design principles allow for the preparation of complex photocatalytic systems, that incorporate efficient molecular catalysts within extended frameworks and that operate in the heterogeneous phase. Some prominent examples have the potential to function as artificial photosynthetic systems, using synergistic effects between photosensitiser-catalysts and sacrificial electron donor/acceptors and which find inspiration from biological systems. The extended systems can lead to charge separations whereby a coordination cluster entity can accumulate oxidation/ reduction equivalents. The network structures generally enable the required charge transport characteristics, whilst deactivations arising from hydrolytic and oxidative degradation require further investigation. In general, MOFs have shown promising turnover characteristics as photocatalysts in energy conversion/storage systems that promote H2O splitting to form O2 and H2 or CO2 reduction. These and other examples point towards intriguing future areas of study and potential applications of photoactive MOFs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ccr.2020.213757.

References


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References


