



Chemical Sensors Based on Metal–Organic Frameworks

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Metal–organic frameworks (MOFs) as chemical sensors have developed rapidly in recent years. There have been many papers concerning this field and interest is still growing. The reason is that the specific merits of MOFs can be utilized to enhance sensitivity and selectivity by various energy/charge transfers occurring among different ligands, ligand, and metal centers, such as from ligands to metal centers or metal centers to ligands, as well as from MOF skeletons to guest species.

This review intends to provide an update on recent progress in various applications of different MOF-based sensors on the basis of their luminescent and electrochemical responses towards small molecules, gas molecules, ions (cations and anions), pH, humidity, temperature, and biomolecules. MOF-based sensors function by utilizing different mechanisms, including luminescent responses of “turn-on” and “turn-off”, as well as electrochemical responses.

Introduction


During the past two decades, metal–organic frameworks (MOFs), also known as porous coordination polymers (PCPs), have experienced explosive growth. MOFs exhibit a wide variety of potential applications in catalysis, gas storage and separation, luminescence, and drug delivery,^[1] owing to their specific features, such as structural diversity, flexibility and tailorability, high porosity, large surface area, and extraordinary adsorption affinities. Among different MOF applications, the MOF-based chemical sensor is clearly a promising application because MOFs can exhibit different degrees of luminescent enhancement or quenching in response to interactions between inserted guest species and the framework. Special features of MOFs include 1) high surface areas would concentrate analytes to high levels, which enhances detective sensitivity; 2) specific functional sites (open metal sites, Lewis acidic/basic sites, and tunable pore sizes) that can realize specific recognition with unprecedented selectivity through host–guest interactions or size exclusion; and 3) flexible porosity or frameworks that enable the reversible uptake and release of substrates to increase regeneration and recycling. In addition to the unique optical properties of MOFs, MOFs as electronic or optoelectronic sensors also exhibit numerous advantages, but this field is still in its infancy and limited examples have been reported.^[2a] A few semiconducting frameworks, or those with redox-active molecules introduced into their pores, are known, such

as HKUST-1 and ZIF-8. MOFs with ordered structures, as determined by the coordination geometry of the metal and the topology of the linkers, can be obtained through rational design. The synthetic flexibility of MOFs allows their intrinsic electrical and optical properties to be tuned, which has been suggested to be easier through theoretical predictions. To date, four kinds of MOFs-based materials have been used as sensors: crystalline MOF materials, MOF-based functional composites, nanoscale MOFs (NMOFs), and MOF membranes. Several general growth methods for the four materials have been developed in recent years, and several excellent review articles on this topic are available.^[2] Herein, we have searched through most current studies to summarize the sensing applications of MOFs. In each part, different mechanisms of responsive signals are discussed based on two visible changes that are induced by the guest molecules adsorbed within the cavity of the MOFs: 1) shift of the emission spectrum or a change in the emitting color; and 2) change in the fluorescence intensity, including luminescent enhancement or quenching, which is defined as “turn-on” and “turn-off” responses, respectively. Recent discoveries and examples of MOF-based sensors are discussed. MOFs are successful in the detection of small molecules, cations, and anions, and to changes in pH, humidity, and temperature. In addition, luminescent MOFs have also been used in the biological field, as exemplified by biosensing and bioimaging applications.^[3]

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Applications of MOF Sensors

Small-molecule sensing

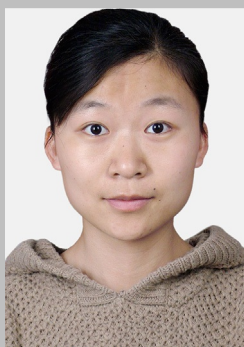
The luminescence detection of trace vapor molecules is always a significant, but challenging task because the vapor pressures of common small organic molecules are usually very low at room temperature. As a result, much less successes have been achieved in the vapor phase than in the corresponding solution. In addition, turn-on response is also more intriguing with more sensitivity and applicability than turn-off.

DMF^[4]

N,N'-Dimethylformamide (DMF) exposure through skin contact and inhalation in various industries can cause serious health concerns for workers, such as hepatotoxicity, embryotoxicity, and carcinogenesis. Song et al. reported a [Eu₂L¹₃(H₂O)₄]₃DMF compound (L¹ = 2',5'-bis(methoxymethyl)[1,1':4',1''-terphenyl]-

4,4''-dicarboxylate) (see Scheme 1 for the structures of the ligands mentioned in this review). After the DMF molecules located in the channels were exchanged by water molecules, its luminescence became very weak. The water-exchanged framework exhibited the capability of selectively sensing DMF vapor with an efficient approximately eightfold turn-on luminescence response.^[4a] Ligand–analyte interactions explain such a turn-on mechanism, which opens up the possibility of building new MOF sensors by designing a suitable ligand. Ye et al. reported another DMF sensor with clear luminescent enhancement

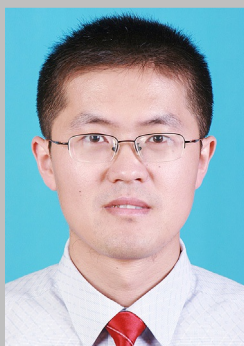
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Prof. Lei Han received his PhD (2005) in physical chemistry under the direction of Prof. Maochun Hong at Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences. Then, he joined the group of Prof. Pingyun Feng at University of California-Riverside (USA) and the group of Prof. Xiaodong Zou at Stockholm University (Sweden) as a Postdoctoral Fellow. He is currently a Professor in the School of Materials Science and Chemical Engineering at Ningbo University (P. R. China). His research focuses on the synthesis and application of inorganic–organic hybrid functional materials.



Prof. Hai-Long Jiang received his PhD in 2008 from the Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences. He worked with Prof. Qiang Xu at the National Institute of Advanced Industrial Science and Technology (AIST; Japan), as an AIST and a JSPS fellow during 2008–2011. Subsequently, he had a postdoctoral stint at Texas A&M University (USA) with Prof. Hong-Cai Zhou. Since 2013, he has been a Full Professor at the University of Science and Technology of China. His interest is in the development of porous materials and nanostructured materials for applications in catalysis and sensing.



caused by reversible crystal-to-crystal transformations compared with other solvents, such as methanol, ethanol, acetone, acetonitrile, tetrahydrofuran, and ethyl acetate.^[4b]

Amines^[5]

Sun et al. detected amine vapors by using a EuL² compound (L² = 4-(pyrimidin-5-yl)benzoic acid).^[5a] An in situ solid-state luminescent sensor setup was designed to test the sensing ability and response rate. EuL² exhibited significant fluorescent quenching for all target amine vapors, such as NH₃·H₂O, CH₃NH₂, C₂H₅NH₂, C₃H₇NH₂, (C₂H₅)₂NH, (C₂H₅)₃N, and aniline, among which the fluorescence quenching of aniline was fastest with a quenching of more than 90% in 10 s. The efficiency of ligand–metal energy transformation affects the emission of the lanthanide compound. The mechanism of the quenching effect can be verified by UV/Vis absorption spectra.

Dincă and co-workers prepared a device by using a new electrically conductive 2D MOF, Cu₃(HITP)₂ (HITP = 2,3,6,7,10,11-hexaminothriphenylene), with a bulk conductivity of 0.2 S cm⁻¹.^[5b] As a reversible chemiresistive sensor, it successfully realized the detection of sub-ppm levels for ammonia vapor through an electrical response. This provides another promising approach to construct new sensing materials through rational syntheses of conductive MOFs.

Volatile organic compounds (VOCs)

Most examples for the recognition of small solvent molecules were reported based on guest-dependent luminescent responses for MOFs;^[6] these can be divided into two categories based on the shift of emission spectrum^[7,8] and a change in the luminescent intensity.^[9–11]

Shift of the emission spectrum

A class of molecules, such as differently functionalized aromatics, can be distinguished by MOF sensors acting as a molecular decoding host with the corresponding readout. Kitagawa and co-workers reported the novel entangled porous zinc-based MOF [Zn₂(bdc)₂(dpNDI)]_n (**1**) (bdc = 1,4-benzenedicarboxylate; dpNDI = *N,N'*-di(4-pyridyl)-1,4,5,8-naphthalenediimide),^[7a] in which dpNDI and bdc moieties are used to enhance the prefer-

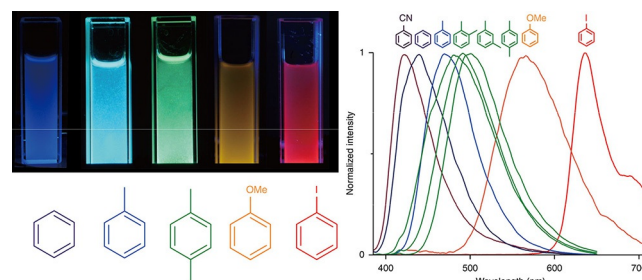
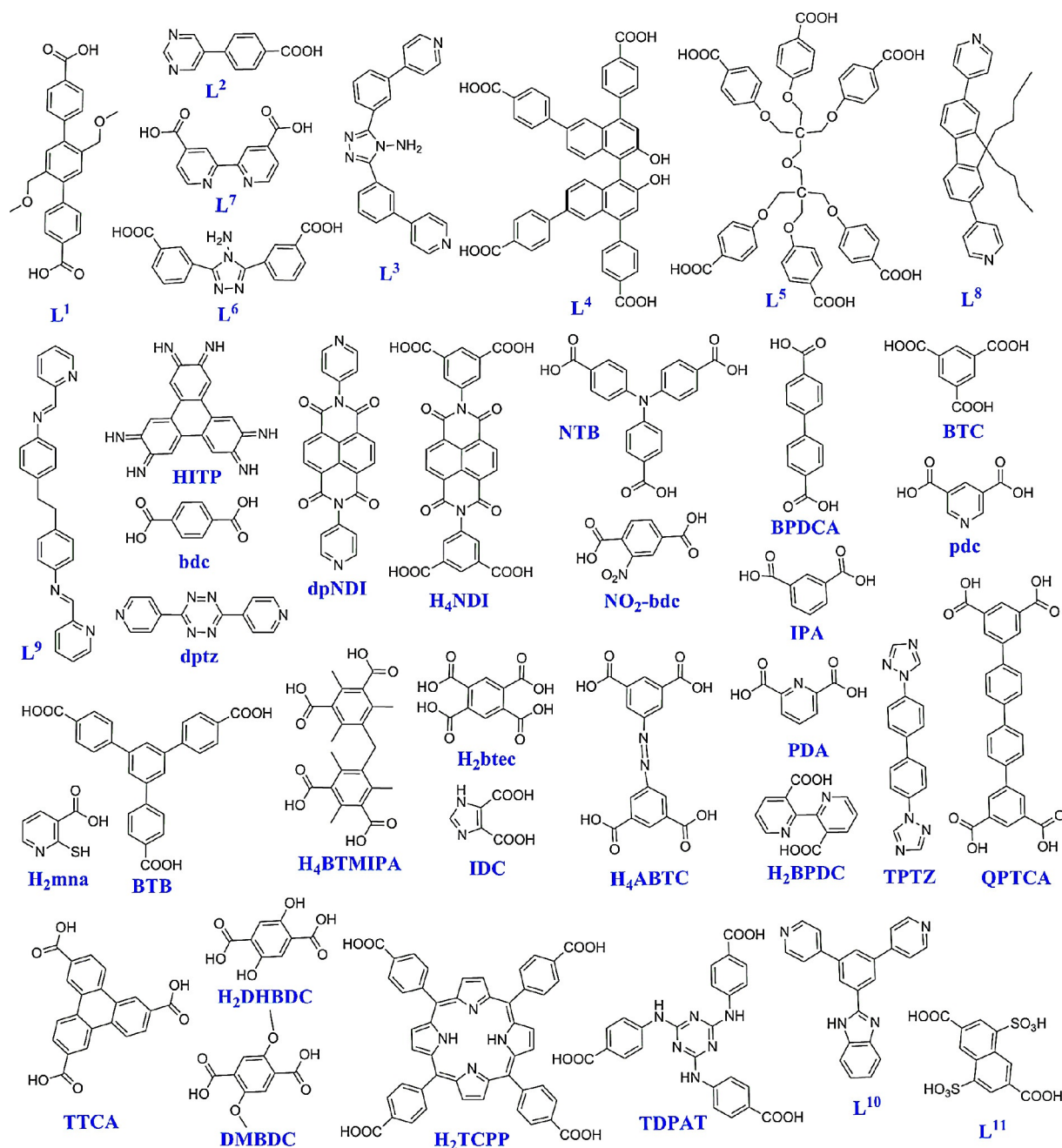


Figure 1. Multicolor luminescence of **1**@VOCs (left) and height-normalized luminescent spectra of **1**@VOCs (right). Reprinted with permission from Ref. [7a]. Copyright 2011 Nature Publishing Group.



Scheme 1. Structures of the ligands mentioned in this review.

ential π - π stacking interactions. This MOF can decode multiple analytes into a corresponding luminescent signal (Figure 1) through particular host-guest interactions based on the crystal-to-crystal transition from a distorted to an undistorted structure. Dong and co-workers prepared another series of photoinduced supramolecular complexes, $Gn \supset CdL_3$ ($L^3 = 4$ -amino-3,5-bis(4-pyridyl-3-phenyl)-1,2,4-triazole; $Gn =$ different substituted aromatics, namely, 2-furaldehyde, 3-furaldehyde, 2-thenaldehyde, 3-thenaldehyde, *o*-toluidine, *m*-toluidine, *p*-toluidine, and aniline), with different crystal colors in a similar single-crystal to single-crystal manner through guest-host interactions.^[7b]

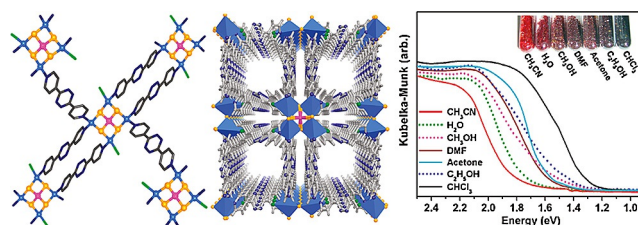


Figure 2. The coordination environment of the $WS_4Cu_4^{2+}$ unit (left), the perspective view of the nanotubular structure (middle), and the UV/Vis spectra and photographs of **2** in various solvents (right). Adapted with permission from Ref. [8a]. Copyright 2011 American Chemical Society.

For the recognition of various VOC molecules, the nanotubular MOF $\{[(WS_4Cu_4)_2(dptz)_3] \cdot 3 DMF\}_n$ (**2**) ($dptz = 3,6$ -di(pyridin-4-yl)-1,2,4,5-tetrazine; Figure 2) was explored by Zheng et al. MOF **2** exhibited different colors, depending on the solvent guests (Figure 2, right).^[8a] Dong et al. reported a solvatochromic sensor with visual color and luminescence responses towards small, polar VOCs.^[8b] The naked-eye and luminescent detection limitations for these VOCs are 5 and 1 ppm, respectively. Another interesting Mg-NDI MOF sensor was prepared by Banerjee and co-workers with a naphthalenediimide (NDI) chromophoric unit ($H_4NDI = N,N'$ -bis(5-isophthalic acid)naphthalenediimide),^[8c] which displayed instant and reversible solvatochromic behavior in the presence of solvents with different polarity, such as dimethyl sulfoxide (DMSO; brown), N,N' -diethylformamide (DEF; dark red), N,N' -dimethylacetamide (DMA; red), acetonitrile (orange). This MOF, with an electron-deficient framework, can also selectively recognize electron-rich organic amines over other functionalized analytes, such as chlorobenzene, toluene, benzene, phenol, 4-nitrophenol, nitrobenzene (NB), and 4-bromotoluene, with an extremely rapid rate at a very low concentration (10^{-5} M). This fact indicated that the interactions between the incorporated solvent and framework were short range and weak, which allowed the external solvents to easily replace the core solvent inside the porous framework.

Change in fluorescence intensity

Chen et al. synthesized a EuMOF sensor, $Eu(BTC)(H_2O) \cdot 1.5 H_2O$ ($BTC = 1,3,5$ -benzenetricarboxylate), with open metal sites.^[9a] This MOF exhibits the most significant enhancing and quenching effects towards DMF and acetone, respectively. The characteristic emission intensity of Eu^{3+} versus the volume ratio of acetone could be well fitted with a first-order exponential decay. Davydovskaya et al. utilized a Cu-BTC thin film to successfully detect different alcohols (methanol, ethanol, 1-propanol, and 2-propanol) at very low concentrations (2–50 ppm) through mass-sensitive (quartz crystal microbalance (QCM)) and work-function-based (Kelvin Probe) readouts.^[10a] A 1,1'-bi-2-naphthol (BINOL)-based chiral CdMOF, $[Cd_2(L^4)(H_2O)_2] \cdot 6.5 DMF \cdot 3 EtOH$ ($L^4H_4 = (R)$ -2,2'-dihydroxy-1,1'-binaphthyl-4,4',6,6'-tetrakis(4-benzoic acid)),^[10b] displayed the ability to act as an enantioselective sensor for 2-amino-3-methyl-1-butanol (AA) with unprecedentedly high Stern-Volmer (SV) constants of up to $31\,200\ M^{-1}$ and an enantiomeric quenching ratio, $K_{SV(S)}/K_{SV(R)}$, of 3.12. Based on the linear relationship between the fluorescence signal and the enantiomeric excess (*ee*) of the analyte, the enantiomeric ratio of a mixture of (*S*)- and (*R*)-AA can be determined in comparison with the calibration curve. The CuMOF-199/single-wall carbon nanotube (SWCNT)-modified electrode, as a novel electrochemical sensor, was fabricated for the simultaneous determination of hydroquinone and catechol, with very low detection limits of 0.08 and 0.1 $mmol\ L^{-1}$, respectively. Other reports of sensors for acetone,^[9] alcohol,^[10] phenol, and aldehyde,^[11] as well as other small molecules,^[12] can be found in the references. We aimed

to be comprehensive, but there must have been other studies that were not included herein.

Explosive compounds

Li and co-workers made a very important contribution to luminescent sensors for explosive and explosive-like molecules.^[13] They provided a donor-acceptor electron-transfer mechanism on the basis of MO and band structure calculations and also published a good review on MOF-based sensors for explosive compounds.

On the basis of the above theory, Yi and co-workers reported an ultrastable CdMOF (**3**) luminescent switch (see Figure 3,

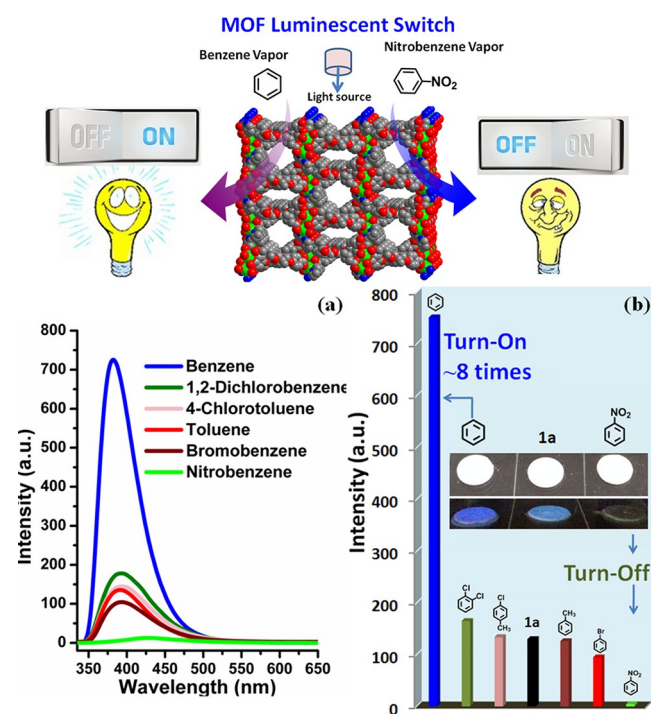


Figure 3. Top: Schematic illustration of a luminescent switch for benzene and NB. Bottom: a) The luminescence spectra and b) the related luminescence intensity of **3**. Reprinted with permission from Ref. [14]. Copyright 2015. The Royal Society of Chemistry.

top) with the flexible H_6L ligand (hexa[4-(carboxyphenyl)oxamethyl]-3-oxapentane acid),^[14] which showed high selectivity and sensitivity for detecting trace amounts of benzene ($[D_6]$ benzene) and NB explosives in the vapor phase through a luminescence enhancement and quenching response, respectively (Figure 3b). The time-dependent enhancing and quenching efficiencies show that the response rate for benzene vapor is 56 s and it exhibits an approximately eightfold fluorescence enhancement in 2–3 min and the fluorescence quenching for NB reaches a maximum in 1 min (Figure 3b). This MOF, with a flexible framework, also exhibits an excellent breathing effect with reversible adsorption behavior for benzene vapor.

It is very intriguing but rather difficult to achieve the selective detection of one specific nitro-explosive molecule in the

presence of other aromatics.^[15] Ghosh and co-workers synthesized the new ZnMOF $[(\text{CH}_3)_2\text{NH}_2]^+[\text{Zn}_4(\mu_4\text{-O})(\text{NTB})_2(\text{NO}_2\text{-bdc})_{0.5}]\cdot 3\text{DMA}$ (**4**) ($\text{NTB} = 4,4',4''\text{-nitrotrisbenzoic acid}$, $\text{NO}_2\text{-bdc} = 2\text{-nitro-4-benzenedicarboxylic acid}$), based on the consideration of energy transfer with a long-range process.^[15a] MOF **4** can selectively detect 2,4,6-trinitrophenol (TNP) in the presence of other nitro compounds, such as 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 1,3-dinitrobenzene (DNB), NB, and nitroaliphatic compounds in CH_3CN through fluorescence quenching at a low concentration (4 mM; Figure 4). Electron- and energy-transfer mechanisms, as well as electrostatic

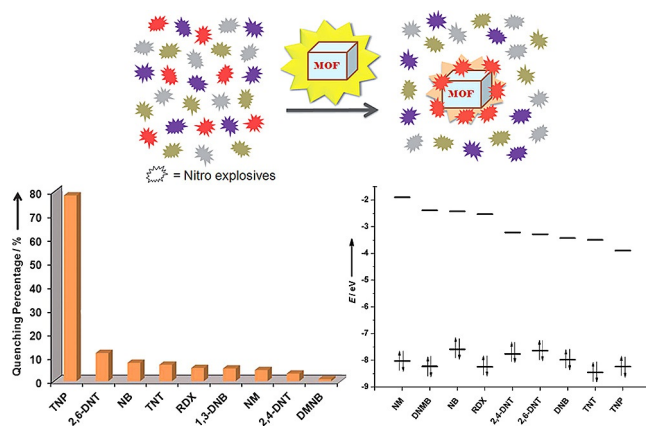


Figure 4. Top: A schematic illustration of the use of MOF-based sensor **4** for the selective detection of target nitro-explosives in the presence of other nitro compounds. The percentage of fluorescence quenching obtained for different analytes (bottom left), and the HOMO and LUMO energies for explosive analytes (bottom right) are shown. Reprinted with permission from Ref. [15a]. Copyright 2013 Wiley-VCH.

interactions between the fluorophore and TNP, explain such selectivity and provide new insights into the design of MOF-based explosive sensors. They improved the water stability and selectivity of the MOF through amine functionalization to form bio-MOF-1 $[(\text{Zn}_8(\text{ad})_4(\text{BPDCA})_6\text{O}\cdot 2\text{Me}_2\text{NH}_2)]\cdot \text{G}$; $\text{G} = \text{DMF}$ and water; $\text{ad} = \text{adeninate}$; $\text{BPDCA} = \text{biphenyl dicarboxylic acid}$),^[15b] which could recognize TNP accurately in aqueous media in the presence of other nitro compounds. These sensors are very important to practical security and environmental applications.

Ion sensing

Cations

Lanthanide cations

MOFs can act as a host and antenna to provide a rigid scaffold that can protect lanthanide cations from solvent quenching and also sensitize them to form tunable fluorescence.^[16] Dong et al. explored a compound of $\{[(\text{Gd}^{\text{III}}_2\text{L}_6)_4\text{Mn}(\text{H}_2\text{O})_6]\cdot x(\text{H}_2\text{O})\}_n$ with encapsulated $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ cations,^[16a] which could sense Eu^{3+} and Tb^{3+} , with their characteristic emission spectra, through reversible and controllable cation exchange. Petoud and co-workers utilized bio-MOF-1 as a host to sensitize visible and near-IR-emitting lanthanide cations in water.^[16b] Yan and

Zhou fabricated a tunable white-light-emitting material based on the Al-MIL-53 nanocrystal with lanthanide(III) cations encapsulated in its channels.^[16c] The groups of Sun and Liu reported the success of Tb^{3+} sensing by using CdMOFs with high sensitivity and selectivity;^[16d,e] Liu et al. found that MgMOF could detect Eu^{3+} .^[16e]

Transition-metal cations

Some transition-metal cations are essential in living biological systems, such as copper(II),^[17] iron(III),^[18] and zinc(II),^[19] but some are toxic and can even cause serious damage to health and the environment, such as chromium(VI), mercury(II), and lead(II).^[20,21] The efficient, straightforward, and real-time detection of trace amounts of transition-metal cations is helpful and much in need.

The pyrene-functionalized microsized MOF particle CPP-16 can selectively detect Cu^{2+} among many other metal ions through a turn-off response (Figure 5).^[17a] $[\text{Eu}(\text{pdc})_{1.5}(\text{DMF})\cdot(\text{DMF})_{0.5}(\text{H}_2\text{O})_{0.5}]$ ($\text{pdc} = \text{pyridine-3,5-dicarboxylate}$),

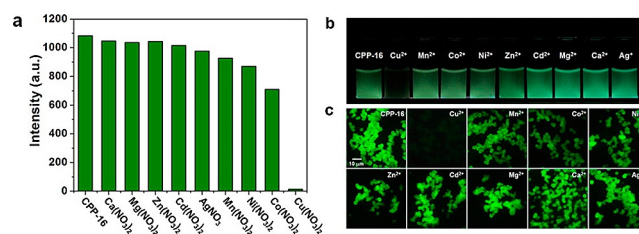


Figure 5. a) Fluorescence intensity changes to CPP-16 after reaction with various metal ions. b) Digital photograph with UV irradiation and c) fluorescence microscopy images of CPP-16 before and after reaction with various metal ions. Adapted with permission from Ref. [17a]. Copyright 2014 American Chemical Society.

with Lewis basic pyridyl sites,^[17b] and $\text{Eu}_2(\text{FMA})_2(\text{OX})(\text{H}_2\text{O})_4\cdot \text{H}_2\text{O}$ ^[17c] ($\text{FMA} = \text{fumarate}$; $\text{OX} = \text{oxalate}$), with mixed ligands, were synthesized by Chen et al. for the sensing of Cu^{2+} in both DMF and aqueous solution. Yang and co-workers fabricated a terbium succinate MOF thin-film sensor through a one-step electrodeposition method; this MOF could sense Cu^{2+} with high sensitivity and selectivity.^[17d]

Additionally, the sensing of Fe^{3+} was achieved by Zhao et al. with $\{[\text{Tb}(\text{BTB})(\text{DMF})\cdot 1.5\text{DMF}\cdot 2.5\text{H}_2\text{O}]_n$ ($\text{BTB} = \text{benzene-1,3,5-tribenzoate}$) based on a drastic fluorescence quenching effect with a high detection limit of $10^{-5} \text{ mol L}^{-1}$ over other various cations, such as Li^+ , Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , Zn^{2+} , Mn^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} , Fe^{2+} , Cr^{3+} , and Cu^{2+} .^[18a] The relationship between the concentration of Fe^{3+} and the quenching effect could not be well fitted by the SV equation, which indicated the coexistence of dynamic and static quenching processes. A EuMOF, $[\text{H}_2\text{N}(\text{CH}_3)_2][\text{Eu}(\text{H}_2\text{O})_2(\text{BTMIPA})\cdot 2\text{H}_2\text{O}$ ($\text{H}_4\text{BTMIPA} = 5,5'\text{-methylenebis(2,4,6-trimethylisophthalic acid)}$), was constructed by Sun et al. that was able to selectively sense Fe^{3+} and Al^{3+} ions from 19 other ions through fluorescence quenching and enhancement, respectively, based on cation exchange between $[\text{H}_2\text{N}(\text{CH}_3)_2]^+$ ions and metal ions.^[18b]

In addition, more turn-on luminescence responses were observed for other metal ions, such as Zn^{2+} ,^[19] Cd^{2+} ,^[20] Hg^{2+} ,^[21] Ag^+ ,^[22] Pb^{2+} ,^[23a,b] Ca^{2+} ,^[23c] Cr^{3+} ,^[23d] Mg^{2+} ,^[23e-g] Mn^{2+} ,^[23h-i] and Al^{3+} .^[23g-m] Two 3d–4f heterometallic coordination polymers ($[Ln(PDA)_3Mn_{1.5}(H_2O)_3] \cdot 3.25 H_2O$; PDA = pyridine-2,6-dicarboxylic acid) were utilized to recognize Zn^{2+} with significant luminescent enhancement,^[19a] this might have resulted from more effective intramolecular energy transfer from the PDA ligand to the Ln^{3+} centers with the addition of Zn^{2+} through a photoinduced electron-transfer (PET) process. A lanthanide-functionalized MOF with encapsulating Eu^{3+} cations in the pores of UiO-66(Zr)-(COOH) could recognize Cd^{2+} in aqueous solution with an eightfold luminescent enhancement, excellent sensitivity (a detection limit of 0.06 nM), and fast response speed (≈ 1 min).^[20a] Adenine-based lanthanide coordination polymer nanoparticles (NPs) showed significant luminescent enhancement for Hg^{2+} with excellent selectivity and ultrahigh sensitivity up to a 0.2 nM detection limit.^[21a] A robust MOF, $Eu^{3+}@MIL-121$ (MIL-121 = $Al(OH)(H_2btec) \cdot H_2O$, H_2btec = pyromellitic acid), showed excellent selective luminescent enhancement for Ag^+ in aqueous solution with fast detection times (< 5 min) and high sensitivity (detection limit, 0.1 nM).^[22a] A DNA-functionalized iron–porphyrinic MOF as an efficient electrochemical sensor could detect Pb^{2+} accurately through an amplified electrochemical signal with a detection limit of 0.034 nM (Figure 6).^[23a] Lanthanide anionic MOFs of $\{K_5[Ln_5(IDC)_4(Ox)_4]_n(20H_2O)_n$ (IDC = imidazole-4,5-dicarboxylate; $Ln = Gd, Tb, \text{ and } Dy$) can sense Ca^{2+} through exchange with K^+ in the channels.^[23c] The sensing of Cr^{3+} was achieved by a microporous anionic ZnMOF,^[23d] namely, $[Zn(ABTC)_{0.5}(NO_3)] [(CH_3)_2NH_2] \cdot DMA \cdot 3H_2O$ ($H_4ABTC = 3,3',5,5'$ -azobenzenetetracarboxylic acid). A detailed analysis of the sensing mechanism was conducted based on various measurement results, such as those from inductively coupled plasma (ICP), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectrometry

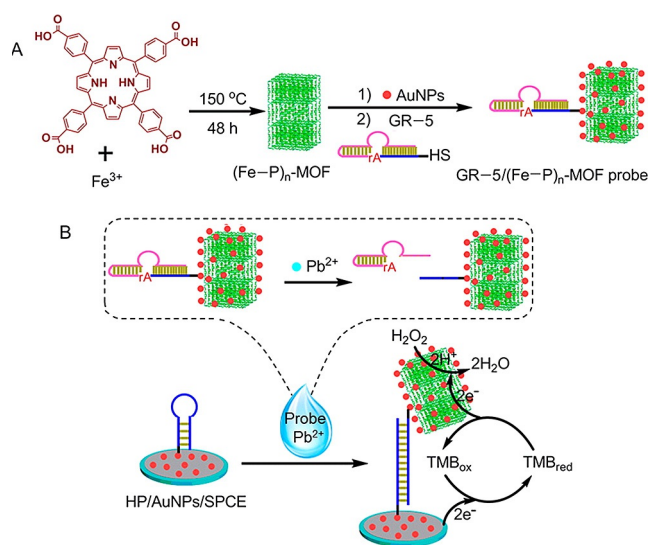


Figure 6. A) Preparation of the GR-5/(Fe-P)_n-MOF probe. B) Electrochemical detection of Pb^{2+} . Adapted with permission from Ref. [23a]. Copyright 2015 American Chemical Society.

(XPS), and UV/vis spectroscopy, which showed that the coordination of Cr^{3+} with the carboxylate oxygen atoms of the framework through d–d transitions was the main reason for selective detection. A UiO-66 optical sensor with hydrophobic chromophore probes (dithizone (DZ)) realized fast kinetic and quantitative detection towards bismuth(III), lead(II), zinc(II), mercury(II), and cadmium(II) at specific pH values.^[23k]

Anions

Various anions, including halogen ions, CN^- , NO_2^- , CO_3^{2-} , PO_4^{3-} , CrO_4^{2-} , and $Cr_2O_7^{2-}$, have been successfully detected by MOF-based sensors.^[24,25] $Tb(BTC)$ with open metal sites, through removing terminal solvent molecules from MOF-76, can recognize F^- with a fourfold luminescent enhancement.^[24a] F^- can also be detected with the lanthanide MOF $[Ln_2(BPDC)(BDC)_2(H_2O)_2]_n$ ($Ln = Eu$ and Tb ; $H_2BPDC = 2,2'$ -bipyridine-3,3'-dicarboxylic acid) with mixed ligands based on a significant decrease in fluorescence.^[24b]

The sensing of CO_3^{2-} was achieved by Yang et al. with a lanthanide mucate coordination polymer ($[Tb(mucate)_{1.5}(H_2O)_2] \cdot 5H_2O$) through the greatest luminescence enhancement over other anions.^[24c] Strong hydrogen-bonding interaction between the numerous OH groups in the mucic acid and CO_3^{2-} reduced vibrational quenching and enhanced the fluorescence. They also synthesized lanthanide MOF-based thin-film materials through electrodeposition in an anhydride system, which was also able to selectively sense CO_3^{2-} from other various anions, such as SO_4^{2-} , PO_4^{3-} , HPO_4^{2-} , ClO_4^- , BrO_3^- , IO_3^- , and halide ions, in aqueous solution through a turn-off response.^[24d]

Two cationic hetero-MOF luminescent probes for I^- ions, namely, $[Ln_2Zn(L^7)_3(H_2O)_4](NO_3)_2 \cdot 12H_2O$ ($Ln = Eu, Tb$; $L^7 = 4,4'$ -dicarboxylate-2,2'-dipyridine anion), were reported; these acted through a turn-off response with NO_3^- counteranions in the channels. The probe exhibited high selectivity and sensitivity (an extremely low detection limit of 0.001 ppm) as well as a fast response time of 10 s.^[24e]

Another heterobimetallic luminescent sensor for CN^- based on the turn-on response was investigated by Lam and co-workers with a Ru^{II} – Cu^{II} donor–acceptor complex ($\{[Ru^{II}(tBubpy)(CN)_4][Cu^{II}(dien)]_2\} [ClO_4]_2$; $tBubpy = 4,4'$ -di-*tert*-butyl-2,2'-bipyridine; $dien =$ diethylenetriamine).^[24f] The luminescence properties of the compound could be restored in the presence of CN^- under a very low detection limit of 1.2 μM (0.03 ppm) in aqueous DMF (Figure 7). Spectroscopic and mass spectrometric studies confirmed that the cyano bridge between Ru^{II} and Cu^{II} was cleaved, assembled to the Cu^{II} centers, and thus produced the luminescent response. Heterobimetallic donor–acceptor complexes can be fine-tuned to produce sensitive chemodosimetric responses to specific analytes.

Cheng and co-workers utilized cationic lanthanide MOFs ($[Ln_4(\mu_3-OH)_4(BPDC)_3(BPDC)_2(H_2O)_6] [ClO_4]_5 \cdot 5H_2O$; $Ln = Tb, Gd$) to sense toxic CrO_4^{2-} with significant quenching over other anions,^[24h] such as F^- , Cl^- , Br^- , I^- , SO_4^{2-} , CO_3^{2-} , NO_3^- , and OAc^- . This is very important and practical because CrO_4^{2-} and $Cr_2O_7^{2-}$ ions are prevalent toxic heavy-metal ions in wastewater

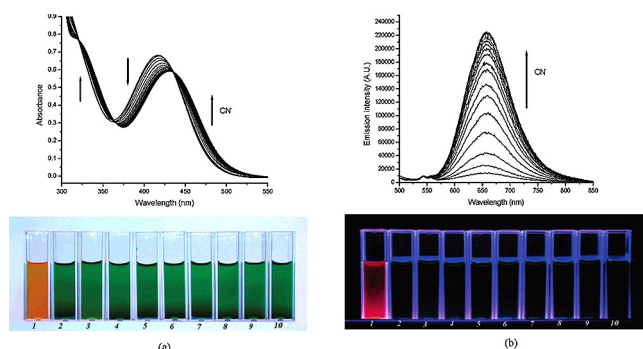


Figure 7. a) Spectroscopic responses and b) UV/Vis spectroscopic titration results and photographs of colorimetric and luminescent responses (bottom). Adapted with permission from Ref. [24f]. Copyright 2004 American Chemical Society

that can accumulate in living organisms; lead to cancer, deformity, and gene mutation; and pose a significant threat to the environment. The detection of trace amounts of $\text{Cr}_2\text{O}_7^{2-}$ was realized through a 2D CdMOF ($[\text{Cd}(\text{TPTZ})(\text{H}_2\text{O})_2(\text{HCOOH})(\text{IPA})_2]_n$; $\text{TPTZ} = \{4-[4-(1H-1,2,4\text{-triazol-1-yl})\text{phenyl}]\text{phenyl}\}-1H-1,2,4\text{-triazole}$; $\text{IPA} = \text{isophthalic acid}$) with similar luminescent quenching.^[24h] Yi and co-workers synthesized a series of flexible CdMOFs for the fast and sensitive turn-off detection of all toxic Cr^{VI} ions containing CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ in aqueous media.^[16d] The cationic fluorene-based Cu^{II} MOF of $[\text{CuL}^8_2(\text{H}_2\text{O})_{0.5}(\text{NO}_3)_2 \cdot 3.25(\text{CH}_2\text{Cl}_2) \cdot (\text{CH}_3\text{OH}) \cdot 0.5\text{H}_2\text{O}]$ was synthesized by Dong et al.^[25a] this exhibited related characteristic colors in response to specific anionic species (Figure 8), such as Cl^- , Br^- , I^- , SCN^- , and N_3^- , by exchanging

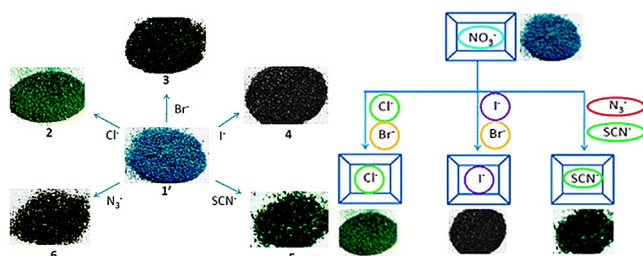


Figure 8. Color changes resulting from anion exchange and anion selectivity. Reprinted with permission from Ref. [25a]. Copyright 2012. The Royal Society of Chemistry.

counteranions with anionic species. This MOF is an excellent naked-eye colorimetric anion sensor. In addition, it can completely separate Cl^-/Br^- , Br^-/I^- , and $\text{SCN}^-/\text{N}_3^-$ anions. Another visual luminescent sensing behavior for various anions was observed with a Cu^{I} MOF through an anion-exchange process.^[25e] Ghosh et al. prepared a homochiral cationic framework ZnMOF, $\{\text{Zn}(\text{T CPP})(\text{OH})_2\}(\text{NO}_3)_2 \cdot x\text{G}_n$ ($\text{H}_4\text{T CPP} = 4,4'-(\text{ethane-1,2-diyl})\text{-bis}(N\text{-pyridin-2-ylmethylene})\text{aniline}$; $\text{G} = \text{solvents}$), which showed interesting anion-dependent tunable luminescence and variable sorption by selective anion-exchange behavior.^[25b]

Gas sensing

Chemical sensors for gas molecules, such as O_2 ,^[26a-e] CO_2 ,^[26f,g] H_2S ,^[27a-d] NO ,^[27e,f] and NH_3 ,^[27g-j] among others,^[27k-m] were developed owing to the importance of environmental monitoring.

Lin et al. constructed three heterobimetallic porous coordination frameworks (5, 6, and 7) by introducing $[\text{Ir}(\text{ppy})_3]$ ($\text{ppy} = 2\text{-phenylpyridine}$) derivatives with highly efficient phosphorescent molecules into a ZnMOF.^[26a] Among them, framework 5 could reversibly sense O_2 based on luminescent quenching because the metal to ligand charge transfer ($^3\text{MLCT}$) phosphorescence from facile intersystem crossing could be readily quenched by molecules with a triplet ground state. Similarly, four lead(II)-iridium(III) heterobimetallic coordination frameworks synthesized by Ho et al. could rapidly detect oxygen with a response time of 50 s and a recovery time of 24 s.^[26b] Lu et al. utilized the methyl viologen cation (MV^{2+}) as a fluorescent material to fabricate the CdMOF $(\text{Me}_2\text{NH}_2)_3(\text{MV})_{1.5}[\text{Cd}_9(\text{TTCA})_8]_{15}\text{EtOH}$ ($\text{TTCA} = \text{triphenylene-2,6,10-tricarboxylate}$), which could stably and selectively sense oxygen within 5 s through a color change detectable by the naked eye (Figure 9).^[26c]

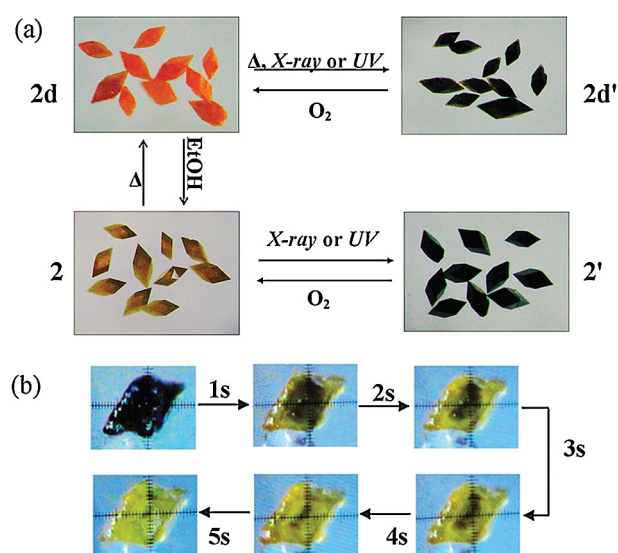


Figure 9. a) Photographic images of the thermo- and photochromic behavior of the CdMOF. b) Photographs of the bleaching process from black to dark yellow by O_2 within 5 s. Reprinted with permission from Ref. [26c]. Copyright 2013. The Royal Society of Chemistry.

The detection of carbon dioxide is very difficult in the presence of other competing gas such as oxygen, water vapor, etc. Jeong et al. selected CDMOF-2 (a γ -cyclodextrin-derived material) with many free primary hydroxyl groups to realize the detection of CO_2 molecules, owing to the reaction of between gaseous CO_2 and the framework carboxylated functionalities.^[26f]

Tang et al. presented the porous nanoscale CuMOF $\{\text{CuL}[\text{A-I OH}]_2\}_n$ ($\text{H}_6\text{L} = \text{meso-tetrakis}(4\text{-carboxylphenyl})\text{porphyrin}$) to realize the real-time in situ detection of H_2S fluctuations in living biological specimens with a rapid response, excellent selectivity.

ty, and hypotoxicity.^[27a] All test results demonstrated that the sensitive biocompatible NMOF fluorescence probe of H₂S provided a great opportunity for the development of probe-based luminescence imaging techniques. Recently, the malonitrile-functionalized ZIF-90 (MN-ZIF-90) was designed and synthesized for quantitative fluorescent detection of H₂S in HeLa cells through significant fluorescence enhancement.^[27b] The nitro-functionalized MOF (UiO-66@NO₂) synthesized by Ghosh et al. also showed a fast and selective fluorescence turn-on response towards H₂S under physiology-mimicking conditions, even in the presence of potentially interfering chemical species, based on reaction-based fluorescence (Figure 10).^[27c] The detection

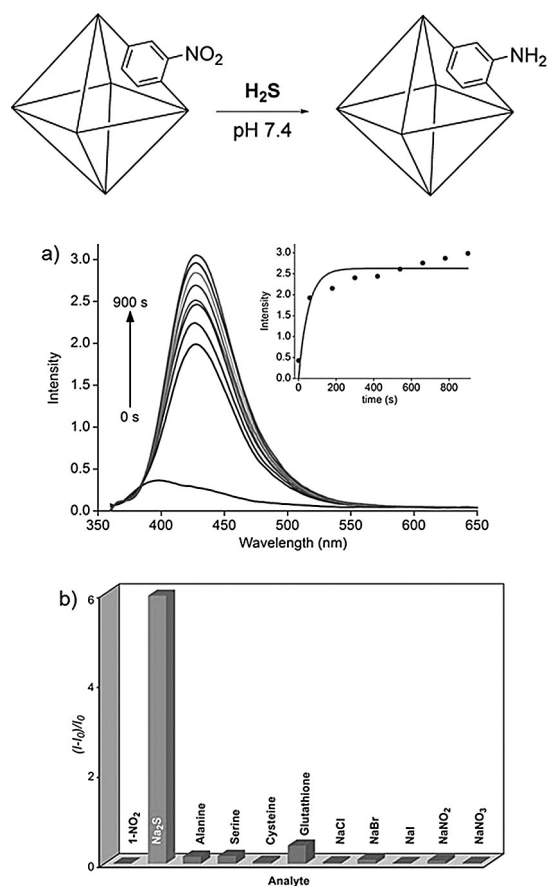


Figure 10. Top: Illustration of a nitro-functionalized MOF as a fluorescence-based turn-on probe for H₂S. a) Time-dependent fluorescence turn-on response upon the addition of Na₂S in HEPES buffer. b) Comparison of the fluorescence turn-on response towards Na₂S and competing biomolecules. Reprinted with permission from Ref. [27c]. Copyright 2015 Wiley-VCH.

limit is the range of H₂S concentrations in biological systems. A similar mechanism was applied by these authors to the detection of NO molecules. They prepared another amine-decorated luminescent MOF UiO-66@NH₂,^[27e] which presented a fast response towards NO with high selectivity and sensitivity in an aerated aqueous medium owing to a deamination reaction of aromatic amines in the presence of NO. The fluorescence of the MOF gradually quenched along with the incremental treatment of NO, even in the presence of other reactive nitrogen

species/reactive oxygen species. The limit of detection was 0.575 mM, which was close to the relevant cellular range of NO. A Cu^{II}-TCA MOF (H₃TCA = tricarboxytriphenylamine) with triphenylamine emitters was assembled by Duan and co-workers.^[27f] The characteristics of such a Cu-TCA are that its emission is very weak, but its fluorescence can be enhanced to approximately 700-fold towards NO, even in the presence of other reactive species, including H₂O₂, NO₃⁻, ONOO⁻, ClO⁻, and O₂. Such luminescent recovery in aqueous solution is attributed to the reducing reaction from quenching Cu^{II} centers to Cu^I ions because of NO coordinated to Cu^{II} centers. The dual emitters from lanthanide and triphenylamine emission make it a ratiometric luminescent sensor towards NO.

The turn-on detection of NH₃ at high temperature was achieved by Dincă et al. with ZnMOF and MgMOF sensors of Zn₂(TCPE) (TCPE = tetrakis(4-carboxyphenyl)ethylene) and Mg(H₂DHBDC) (H₂DHBDC²⁻ = 2,5-dihydroxybenzene-1,4-dicarboxylate),^[27g] these displayed a significant shift in the emission maximum. The electrochemical response for formaldehyde was reported by using a traditional semiconducting ZIF-67 with a fast response at a low operating temperature (150 °C) and a low detection limit of 5 ppm.^[27j]

Biosensing

As mentioned previously, MOF-based sensors have proved to be an effective method to sense NO and H₂S under biological conditions. This section focuses on the sensing of biological molecules, such as human serum albumin, bacterial endospores, and cancer cell apoptosis.^[28,29]

Lin et al. assembled a series of new core-shell nanocomposites with a NMOF core^[28a] and a silica shell through four steps: first, the synthesis of the Ln(BDC)_{1.5}(H₂O)₂ NMOF **8** (Ln = Eu³⁺, Gd³⁺, or Tb³⁺); second, construction of poly(vinylpyrrolidone) (PVP)-functionalized Ln(BDC)_{1.5}(H₂O)₂ NPs (**9**); third, silica-coated NMOF (**10**) with the desired shell thickness was formed; and fourth, further functionalization of the silica surface with a silylated Tb-EDTA monoamide (Tb-EDTM; EDTA = ethylenediaminetetraacetic acid) derivative formed the **10'**-Tb-EDTM monoamide composite. The final NMOF composite exhibited a turn-on luminescent response towards dipicolinic acid (DPA; a major constituent of many pathogenic spore-forming bacteria) owing to the formation of the Tb-EDTM-DPA complex. Such ratiometric sensors also display excellent selectivity in the presence of other biologically prevalent interferences. Another NMOF of Eu₂(FMA)₂(OX)(H₂O)₄·4H₂O (FMA = fumarate, OX = oxalate) was synthesized by Qian and co-workers,^[28b] this NMOF also achieved the highly selective, sensitive, and instant detection of DPA through a significant luminescent enhancement by approximately 90 times for 2 ppm DPA (Figure 11).

A MOF-based biosensor for double-stranded DNA (ds-DNA) in vitro was developed,^[28c] in which *N,N*-bis(2-hydroxyethyl)di-thiooxamidatocopper(II) (H₂dtoaCu) MOF was a platform to absorb a dye-labeled triplex-forming oligonucleotide (TFO) probe to quench its fluorescence owing to a PET process. Nevertheless, the fluorescence could be recovered once the target

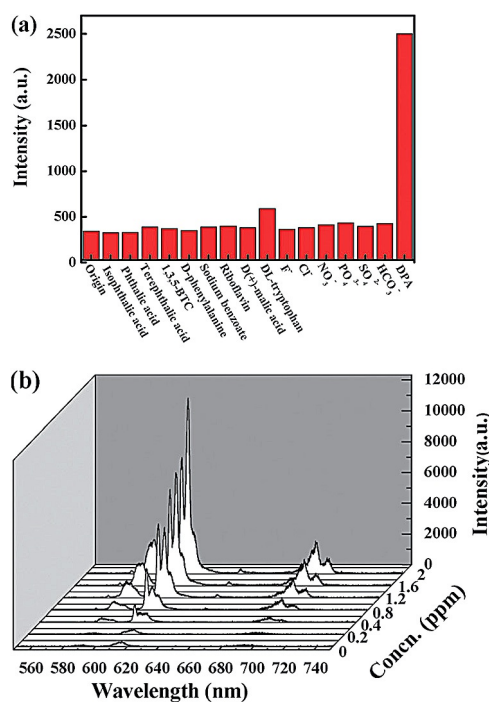


Figure 11. a) The intensities of a solution of NMOF **8** hexagonal nanoplates in ethanol with 1.0 ppm of different analytes. b) Photoluminescence spectra of a solution of NMOF **8** in ethanol with the addition of different concentrations of DPA. Reprinted with permission from Ref. [28b]. Copyright 2012. The Royal Society of Chemistry.

ds-DNA was added because the TFO probe was released from the MOF platform and interacted with DNA. It is a simple, cost-efficient luminescent sensor that can recognize ds-DNA with high sensitivity and selectivity. An amine-functionalized MOF (UiO-66-NH₂) was employed by Jiang et al. as an effective fluorescent sensing platform for DNA detection.^[28d] They also found that the MOF could distinguish complementary and mismatched DNA sequences with high selectivity and sensitivity. Hydrogen-bonding interactions between the MOF host and single-stranded DNA (ssDNA) might explain such DNA detection. In addition to fluorescence sensors, a MOF-based electrochemical sensor was also designed for DNA detection. Lei et al. fabricated FeTCPP@MOF composites (Figure 12),^[28e] in which iron(III) *meso*-5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin chloride (FeTCPP) was encapsulated into HKUST-1 (Cu₃(BTC)₂), then conjugated with a recognition element for streptavidin (SA) in a one-step process. The composites could detect target DNA down to 0.48 fm through the enhancement of the electrochemical signal. Lei and co-workers adopted a similar assembly method to construct another PS@MOF nanocomposite,^[28f] in which a porphyrin derivative, tetrakis(1-methylpyridinium-4-yl)porphyrin (TMPyP), and the photosensitizer (PS) were incorporated into the cage of HKUST-1. The PS@MOF as a nanoprobe achieved high efficiency in cancer therapy and in situ therapeutic monitoring with caspase-3 activation. Additionally, electrochemical sensing for nonenzymatic glucose was also reported with nickel(II)-based metal-organic coordination polymer nanoparticle (NICPNP)/reduced graphene oxide (rGO) nanocomposites.^[28g]

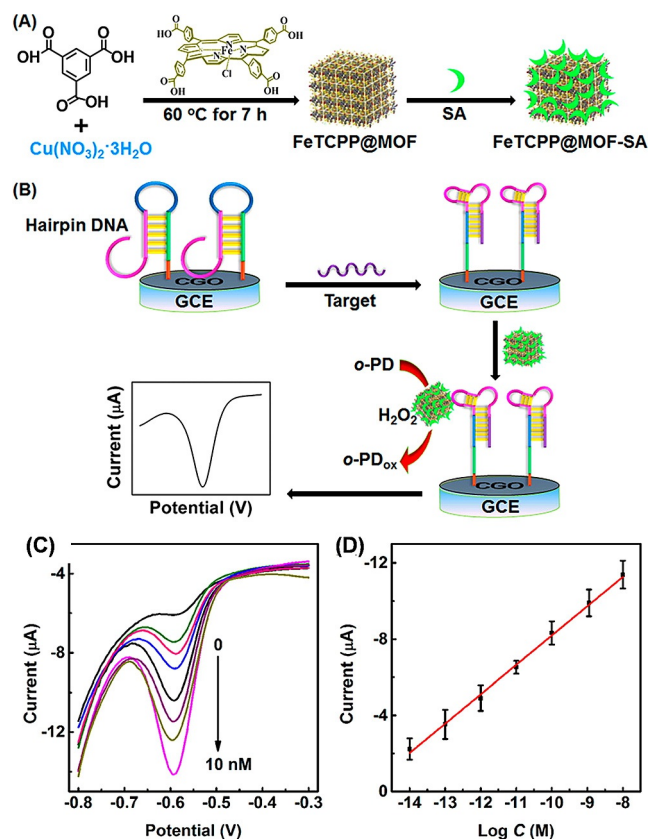


Figure 12. A) Scheme for the synthesis of the FeTCPP@MOF-SA composite. B) Electrochemical DNA sensing through allosteric switching of hairpin DNA. C) Differential pulse voltammetry (DPV) responses of FeTCPP@MOF-SA to target DNA at concentrations of 0, 10 fM, 100 fM, 1 pM, 10 pM, 100 pM, 1 nM, and 10 nM (from top to bottom). D) Calibration curve of current intensity versus the logarithmic value of DNA concentration. Adapted with permission from Ref. [28e]. Copyright 2015 American Chemical Society.

Sensing of humidity

MOF-based sensors operating through changes to fluorescence or electrochemical signals have also been successfully applied to humidity measurements.^[30] Dong et al. reported a naked-eye colorimetric sensor for humidity with CuMOF.^[30a] The color of these crystals changed to red-brown from bright yellow above 33% relative humidity (RH), and the luminescent intensity was gradually quenched by encapsulated water molecules after different times owing to nonradiative energy transitions (Figure 13). Another LnMOF humidity sensor was also synthesized by them with the heteroatom-rich mixed-ligand system of pyridyl-4,5-imidazole dicarboxylic acid and oxalic acid.^[30b] The switching on and off of fluorescence for Ln³⁺ emitters can be controlled by adsorbed and desorbed water based on O–H vibrational quenching.

A thin film of HKUST-1 was prepared by the groups of Qiu^[30c] and Robinson^[30d] to be applied for the detection of water vapor. Qiu et al. utilized a method of homogenous nucleation to prepare a large-scale continuous thin film of HKUST-1 on a polished copper slice (Figure 14a–d).^[30c] The film sensor exhibited high sensitivity and repeatability based on the humidity capacitance signal in the reverse order of humid-

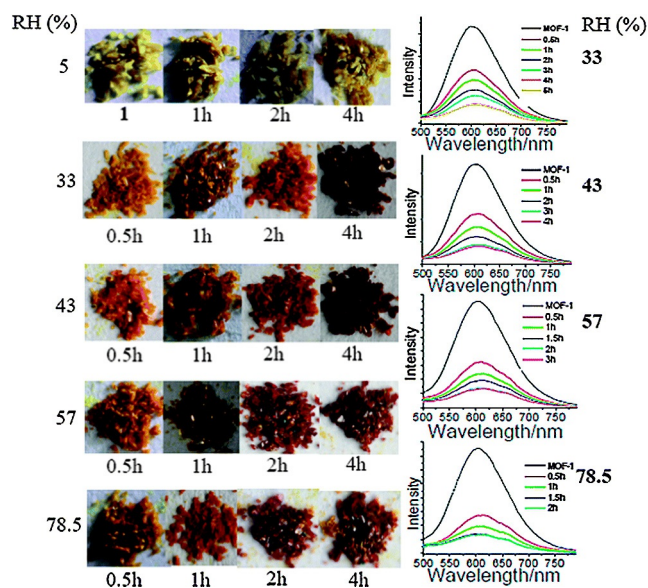


Figure 13. Left: Photographs showing the color changes of the bulk crystal samples of CuI/MOF in different atmospheres with different RH. Right: The corresponding solid-state emission spectra of CuI/MOF in different atmospheres with different RH (33–78.5%). Reprinted with permission from Ref. [30a]. Copyright 2014 The Royal Society of Chemistry.

ification and desiccation processes for RH values of 11.3, 32.8, 57.6, 75.3, and 84.3%, with a rapid response and recovery time (Figure 14e). Robinson and co-workers prepared a MOF-functionalized electrochemical sensor by growing a Cu-BTC film on a surface acoustic wave (SAW) by using a layer-by-layer (LBL) growth procedure to achieve the detection of water vapor at sub-ppm concentrations.^[30d]

Ruan et al. reported that amine-functionalized titanium MOF NPs (NH₂-MIL-125(Ti)) were coated on interdigitated electrodes for humidity sensing based on the changes to the impedance.^[30e] Manos et al. reported that MgMOF as an efficient sensor capable of rapidly detecting traces (0.05–5% v/v) of water in different organic solvents based on the sensing mechanism turn-on fluorescent enhancement.^[30f]

pH sensing

The pH plays an essential role in regulating cellular behavior. Fluorescence-based pH probes are highly desirable because they may rapidly monitor minor pH changes in biological environments and are usually nondestructive to cells.^[31] Rocha et al. reported a luminescent pH sensor composed of [Eu₃(C₁₄H₆N₂O₄)₄(OH)(H₂O)₄·2H₂O] with a linear photoluminescence response within the pH range of 5–7.5.^[31a] The most interesting thing was that as a miniaturized pH sensor it achieved the self-calibration of the emitting signal.

An exceptionally stable porphyrinic zinc MOF (PCN-225 = Zr₆(μ₃-O)₄(μ₃-OH)₄(OH)₄(H₂O)₄(H₂TCPP)₂) as a promising pH sensor was synthesized by Jiang et al. with exceptional chemical stability in aqueous solutions over a wide pH range from 1 to 11.^[31b] The luminescence intensity rose with increasing pH over the whole experimental range (0–10.2). In particular, over

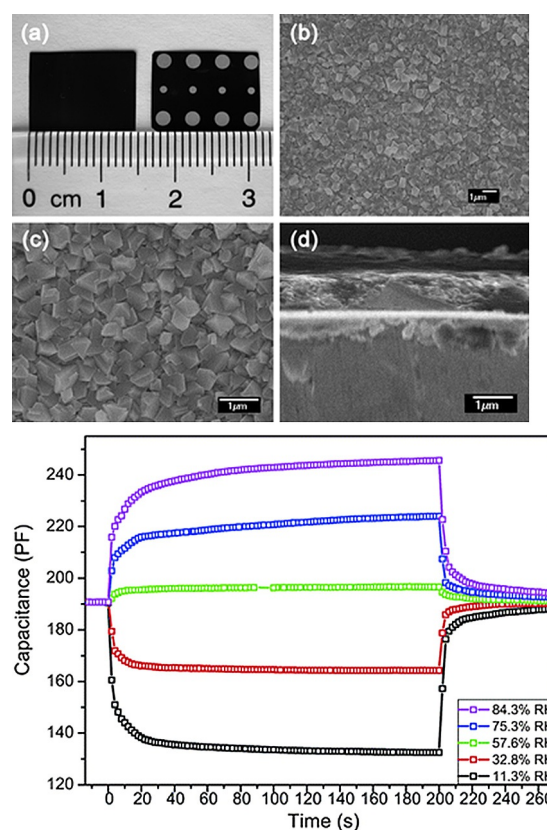


Figure 14. Top: a–d) Photographs and SEM images of an as-prepared film of Cu₃(BTC)₂. Bottom: Temporal response to different RH values of the film sensor. Reprinted with permission from Ref. [30c]. Copyright 2011 The Royal Society of Chemistry.

the pH range of 7–10, the fluorescence intensity exhibited a close correlation with pH variation. Additionally, visual pH sensing was achieved with another water-stable zirconium porphyrin MOF (PCN-222) based on a distinct reversible colorimetric and fluorescent turn-off/turn-on pH response over the range of 0–6.^[31c] UiO-66-N=N-ind (UiO-66-N=N-ind_{1h} and UiO-66-N=N-ind_{3h}) materials were synthesized by a postsynthetic modification (PSM) diazotization strategy to improve UiO-66-NH₂. The UiO-66-N=N-ind_{3h} sample exhibited a pH-dependent fluorescence over the wider range of 1–12, compared with a range of 1–9 for UiO-66-NH₂.^[31d] Lin et al. first used a new F-UiO NMOF, in which fluorescein isothiocyanate (FITC) was conjugated to the bridging ligands of UiO NMOF by covalent bonds, to give exceptional real-time intracellular pH sensing in live cells.^[31e] This provided an excellent tool for studying NMOF–cell interactions.

Temperature sensing

The temperature-dependent luminescence is a very common phenomenon, which has been utilized to develop luminescent thermometers. The change of fluorescence intensity of MOFs as the temperature varies is one method. Another method is to construct dual-emitting MOFs with codoped lanthanide compounds or introducing fluorescent materials such as dye

molecules as ratiometric thermometers. Qian et al. made a prominent contribution to this field and summarized the progress of MOF-based thermometers.^[32] Some of the latest reports have been updated in review articles.^[33,34]

The temperature-dependent luminescent behavior based on mixed lanthanide MOFs, namely, $\text{Eu}_{0.0069}\text{Tb}_{0.9931}\text{-DMBDC}$ (DMBDC = 2,5-dimethoxy-1,4-benzenedicarboxylate), was reported by Chen et al.,^[33a] in which the luminescent intensity of the Tb^{3+} center decreases, but that of Eu^{3+} increases as the temperature increases. All luminescent intensities of Tb^{3+} and Eu^{3+} decrease gradually in Tb-DMBDC and Eu-DMBDC with increasing temperature owing to the thermal activation of non-radiative decay pathways. Since then, more mixed-lanthanide MOFs have been constructed as luminescent thermometers for different temperature ranges based on similar luminescent behavior.^[33] The use of codoped LnMOFs as ratio- and colorimetric luminescent thermometer is unquestionable because they are not restricted by the concentration of luminescent centers or optoelectronic drifts of the excitation source and detector.

Additionally, Wolfbeis and co-workers found that a single LnMOF could also act as an excellent luminescence thermometer based on changes to the luminescence intensity, which might be easily detected.^[34a] They prepared terbium tris[(2-hydroxy-benzoyl)-2-aminoethyl]amine (Tb-THBA) NPs. The luminescent intensity exhibited a significant temperature dependence over the range of 20–65 °C (Figure 15). EuMOF NPs (Eu

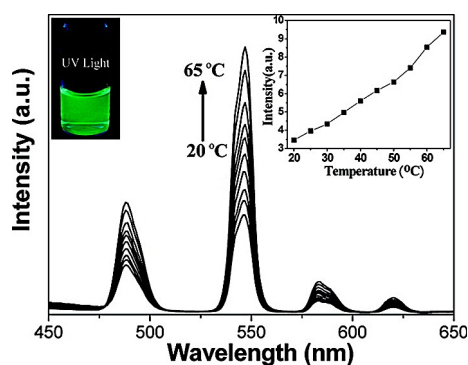


Figure 15. Luminescence spectra as a function of temperature and a photograph of Tb-THBA NPs in an aqueous dispersion. Adapted with permission from Ref. [34a]. Copyright 2010 American Chemical Society.

tris(dinaphthoylmethane)-bis(triethylphosphine oxide)) were also synthesized by Wolfbeis et al. with decreasing fluorescence intensity as the temperature increased from 10 to 50 °C.^[34b] The sensing resolution could be up to approximately 0.3 °C through the combination of fluorescence intensity and lifetime data because it is known that only intensity-based measurements might suffer from variation of the sensor concentration and drifts of the optoelectronic system (lamps and detectors).

Apart from the above mixed- and single-lanthanide MOFs, ratiometric temperature sensing may be achieved by dual emitters composed of organic dyes and lanthanide ions because energy transfer between luminescent guest species and lanthanide ions can be theoretically tuned through the inclu-

sion of different luminescent guest species based on spectral overlap. A ZJU-88 perylene composite ($\text{ZJU-88} = [\text{Eu}_2(\text{QPTCA})(\text{NO}_3)_2(\text{DMF})_4] \cdot (\text{CH}_3\text{CH}_2\text{OH})_3$; QPTCA = 1,1':4',1''':4''',1''''-quaterphenyl-3,3''',5,5''''-tetracarboxylic acid) was fabricated by Qian et al.,^[34c] this composite exhibited high sensitivity towards temperature owing to its unique energy transfer between perylene molecules and lanthanide centers. The linear relationship between the intensity ratio of Eu^{3+} ions and perylene, as well as temperature, could be observed over the range of 20 to 80 °C.

Transition-metal MOFs can also detect temperature. A ZnMOF ($[\text{Zn}_2(\text{TDPAT})(\text{H}_2\text{O})_3]$; TDPAT = 2,4,6-tris(3,5-dicarboxylphenylamino)-1,3,5-triazine) was constructed by Shi et al.^[34d] to quantitatively detect temperature from 164 to 276 K; the luminescence intensity increased with cooling temperature. Sun and co-workers constructed a $\text{Ag}_6\text{-Zn}^{II}$ heterometallic aggregate, $(\text{NH}_4)_2\{[\text{Zn}_2(\text{phen})_2(\text{H}_2\text{O})_4][\text{Ag}_6(\text{mna})_6]\} \cdot 2\text{H}_2\text{O} \cdot 2\text{CH}_3\text{CH}_2\text{OH}$ ($\text{H}_2\text{mna} = 2\text{-mercaptopyridine}$, phen = 1,10-phenanthroline),^[34e] which exhibited interesting temperature-dependent photoluminescence behavior, including gradual redshifts from $\lambda = 544$ to 565 nm in the emission position and a dramatic enhancement in luminescent intensity from 298 to 77 K.

Summary and Outlook

The objectives of this review were to provide a summary and classification for various MOF-based sensors operating under different mechanisms of luminescent and optoelectronic responses (Table 1).

It is well known that luminescent MOFs show great promise as various types of sensor owing to their remarkable structural diversity and tunable luminescent properties. The majority of luminescent-based MOF sensors operate by the turn-off mechanism of fluorescent quenching, and much fewer reports are based on the turn-on mechanism, including the luminescent enhancement or shift of the emission (color change). The turn-on detection is more sensitive with lower detection limits because the naked eye can quickly recognize the strong emission and color change in the visible range from a previously dark background or originally low- and non-emitting MOF. In addition, it also exhibits better selectivity because the shift of the emission peak is frequently specific towards target guest molecules based on guest–host chemistry. More sensors can be fabricated for the turn-on mechanism by designing a host material with stronger interactions towards a particular analyte. Electron and energy transfer between the analyte molecule and related MOF frameworks is the major contribution for luminescent and electronic responses. Theoretical calculations can effectively predict host–guest interactions and improve the design of the structure of MOFs.

Apart from luminescent responses, some new emerging opportunities were found for using MOFs as electronic or optoelectronic sensors through transduction mechanisms because the features of long-range order and synthetic flexibility of the MOF in a predetermined spatial orientation could be tuned for specific properties. MOFs with good electric conductivity are still very few because of the poor conductivity of organic link-

Table 1. A summary of the luminescent or electrochemical response and sensing applications of selected MOFs.

Response mechanism	MOFs	Ligands	Target	Ref.	
turn-on shift of emission	$[Zn_2(bdc)_2(dpNDI)]_n$	bdc, dpNDI	functionalized aromatics	[7a]	
	CdL^3_2	$L^3 = 4\text{-amino-}3,5\text{-bis(4-pyridyl-3-phenyl)-}1,2,4\text{-triazole}$		[7b]	
	$[Zn_3(OH)_2(btca)_2] \cdot DMF \cdot 4H_2O$	$H_2btca = \text{benzotriazole-5-carboxylic acid}$		[7c]	
	OH-MOF-74	$(E)\text{-}3\text{-}(2\text{-hydroxyl-phenyl})\text{acrylic acid}$		[7d]	
	$[Cd(CIO_4)_2(L^3)_2] \cdot 2CH_2Cl_2$	$L^3 = 4\text{-amino-}3,5\text{-bis(4-pyridyl-3-phenyl)-}1,2,4\text{-triazole}$		[8k]	
	$\{[(WS_4Cu_4)_2(dptz)_3] \cdot 3DMF\}_n$	dptz	VOC molecules	[8a]	
	$H_2OCu_2(L^{10})_2$	$L^{10} = 1\text{-benzimidazolyl-}3,5\text{-bis(4-pyridyl)benzene}$		[8b]	
	$[Zn_7(ip)_{12}(OH)_2]$	Hip = 1 <i>H</i> -imidazo[4,5- <i>f</i>][1,10]phenanthroline		[8d]	
	NUS-1a	4,4'-(2,2-diphenylethene-1,1-diyl)dibenzoic acid		[8g]	
	$[Zn_4O(\text{benztb})(\text{btb})_{2/3}]$	benztb = <i>N,N,N',N'</i> -benzidinetetrabenzoate		[8f]	
	$[Zn_4(\text{dmf})(\text{ur})_2(\text{ndc})_4]$	ndc = 2,6-naphthalenedicarboxylic acid, ur = urotropin		[8h]	
	$[In_2(OH)_2(TBAPy)] \cdot (\text{guests})$	TBAPy = 1,3,6,8-tetrakis(<i>p</i> -benzoic acid)pyrene		[8j]	
	$Zn_2(C_{30}H_{16}O_8)(H_2O)_2 \cdot 4DEF$	$C_{30}H_{16}O_8 = \text{tetrakis(4-carboxyphenyl)ethylene}$	organic amines	[8e]	
	Mg-NDI	NDI		[34c]	
	$[Cd_8(p\text{-ClPhHIDC})_{12}(4,4'\text{-bipy})_6]$	$p\text{-ClPhH}_3\text{IDC} = (4\text{-chlorophenyl})\text{-}1H\text{-imidazole-}4,5\text{-dicarboxylic acid}$	pyridine	[12q]	
$\{[Cu(\text{pytpy})] \cdot NO_3 \cdot CH_3OH\}_n$	pytpy = 2,4,6-tris(4-pyridyl)pyridine	different ions	[25e]		
increasing luminescent intensity	$[Eu_2L^1_3(H_2O)_4] \cdot 3DMF$	$L^1 = 2',5'\text{-bis(methoxymethyl)-}[1,1':4',1''\text{-terphenyl]-}4,4''\text{-dicarboxylate}$	DMF vapor	[4a]	
	$\{[Ln(OAc)_2(H_2O)(OBPT)] \cdot 3H_2O\}_n$	HOBPT = 4,6-bis(2-pyridyl)-1,3,5-triazin-2-ol	DMF solution	[4b]	
	$\{[Me_2NH_2]_{0.125}[Ln_{0.125}(H_2L^{11})_{0.25}] \cdot xDMF\}_n$	$H_4L^{11} = 4,8\text{-disulfonyl-}2,6\text{-naphthalenedicarboxylic acid}$	Tb^{3+}	[16l]	
	CdMOFs	$H_6L^5 = \text{hexa[4-(carboxyphenyl) oxamethyl]-}3\text{-oxapentane acid}$	Tb^{3+}	[16d]	
	$\{[La_2(PDA)_3(H_2O)_4] \cdot H_2O\}_\infty$	H_2PDA	Pb^{2+}, Ca^{2+}	[20c]	
	$Zn(\text{btdb})(\text{DMA}) \cdot H_2O$	btbd = 4,4'-(benzothiadiazole-4,7-diyl)dibenzoate	Cd^{2+}	[20d]	
	$Eu^{3+} @ UiO\text{-}66(\text{Zr})(\text{COOH})_2$	bdc	Cd^{2+}	[20a]	
	$\{Ru^{II}(\text{rBubpy})(\text{CN})_2[(\text{CN})Cu^{II}(\text{dien})L]_2\}^{2+}$	rBubpy, dien	CN^-	[24f]	
	$[Zr_6O_4(OH)_4(NO_2\text{-bdc})_6]_n$	$NO_2\text{-bdc}$	H_2S	[27c]	
	Cu-TCA	H_3TCA	NO	[27f]	
	turn-off luminescent quenching	$\{[EuL^2_2(H_2O)_3](NO_3)\}$	$HL^2 = 4\text{-}(pyrimidin\text{-}5\text{-yl})\text{ benzoic acid}$	amine vapors	[5a]
		$[Eu_3(\text{bcbp})_3(NO_3)_7(OH)_2]_n$	$H_2\text{bcbp} \cdot 2Cl = 1,1'\text{-bis(4-carboxyphenyl)(}4,4'\text{-bipyridinium) dichloride}$	amine solutions	[5h]
$[Li_2(H_2\text{pml})] \cdot C_4H_8O_2$		$H_4\text{pml} = 1,2,4,5\text{-benzenetetracarboxylic or pyromellitic acid}$	NB	[8i]	
$[Eu(\text{BTPCA})(H_2O)] \cdot 2DMF \cdot 3H_2O$		$H_3\text{BTPCA} = 1,1',1''\text{-}(benzene\text{-}1,3,5\text{-triy})\text{tripiperidine-}4\text{-carboxylic acid}$	Fe^{3+}	[18g]	
$\{[Tb(\text{BTB})(\text{DMF})] \cdot 1.5DMF \cdot 2.5H_2O\}_n$		BTB	Fe^{3+}	[18a]	
$[Ln(\text{BTATB})(\text{DMF})_2(H_2O)] \cdot \text{DMF} \cdot 2H_2O$		$H_3\text{BTATB} = 4,4',4''\text{-}[benzene\text{-}1,3,5\text{-triy}(\text{triazanediyl})]\text{tribenzoate}$	Zn^{2+}	[19d]	
MIL-53(Fe)	bdc	Hg^{2+}	[21b]		
UiO-66@NH ₂	bdc	NO gas	[27e]		
electrochemical response	ZnO@ZIF-8 nanorods	2-methylimidazole	H_2O_2	[12r]	
	GR-5/(Fe-TCPP) _n -MOF	TCPP = 5,10,15,20-tetrakis(4-carboxyl)-21 <i>H</i> ,23 <i>H</i> -porphyrin	Pb^{2+}	[23a]	
	MOF-5 thin films	bdc	ascorbic acid	[25j]	
	HKUST-1-GO composites	BTC	ammonia	[27i]	
	ZIF-67	2-methylimidazole	formaldehyde gas	[27j]	
	$Cu(\text{bdc}) \cdot xH_2O$	bdc	humidity	[30j]	
$NH_2\text{-MIL-}125(\text{Ti})$	$NH_2\text{-bdc} = 2\text{-aminoterephthalic acid}$	humidity	[30e]		

ers in the MOF structures. However, MOF-based thin films or NPs deposited on a variety of substrates, as well as incorporating other conductive materials into the channels, may improve their conductivity. Some MOF-based sensors discussed herein have been successfully applied as electrochemical sensors with excellent results. However, the field of MOF-based electrochemical sensors is still very new, and related reports are very limited.

To further improve the detecting ability and directional selectivity of sensors, various functional MOFs have been successfully constructed, such as MOF NPs, MOF thin films, and functionalized MOFs modified by specific organic groups. The in-depth analysis of the sensing mechanism is the most fundamental thing to achieve the controllable syntheses of MOF sensors with high selectivity for target compounds. Some relationships between structure and luminescent behavior have

been revealed through theoretical methods. Based on theoretical results, the direction of charge/energy transfer between MOFs and analyte can be confirmed, so it will be feasible to realize controlled luminescent changes through adjusting the electronic structure with specific functional groups, and further achieve MOF sensor materials through rational design. This is a very important yet challenging issue because of the difficulty in forming target products because these are affected by various factors. In addition, some issues during practical applications still need to be improved; these include the stabilities of recycling, the cost of materials, and portability. Therefore, continuous efforts will be invested in this field, especially for MOF-based electrochemical sensors based on MOF NPs and membranes, which are still in their infancy.

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- [1] a) N. C. Burtch, H. Jasuja, K. S. Walton, *Chem. Rev.* **2014**, *114*, 10575–10612; b) Y. Cui, Y. Yue, G. Qian, B. Chen, *Chem. Rev.* **2012**, *112*, 1126–1162; c) P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. E. Morris, C. Serre, *Chem. Rev.* **2012**, *112*, 1232–1268; d) H.-L. Jiang, Q. Xu, *Chem. Commun.* **2011**, *47*, 3351–3370; e) H.-Q. Xu, J. Hu, D. Wang, Z. Li, Q. Zhang, Y. Luo, S.-H. Yu, H.-L. Jiang, *J. Am. Chem. Soc.* **2015**, *137*, 13440–13443; f) Q. Yang, Q. Xu, S.-H. Yu, H.-L. Jiang, *Angew. Chem. Int. Ed.* **2016**, *55*, 3685–3689; *Angew. Chem.* **2016**, *128*, 3749–3753; g) G. Huang, Y.-Z. Chen, H.-L. Jiang, *Acta Chim. Sin.* **2016**, *74*, 113–129.
- [2] a) V. Stavila, A. A. Talin, M. D. Allendorf, *Chem. Soc. Rev.* **2014**, *43*, 5994–6010; b) X. Zhang, W. Wang, Z. Hu, G. Wang, K. Uvdal, *Coord. Chem. Rev.* **2015**, *284*, 206–235; c) M. Y. Masoomi, A. Morsali, *Coord. Chem. Rev.* **2012**, *256*, 2921–2943; d) W. Li, Y. Zhang, Q. Li, G. Zhang, *Chem. Eng. Sci.* **2015**, *135*, 232–257; e) O. Shekhah, J. Liu, R. A. Fischer, C. Wöll, *Chem. Soc. Rev.* **2011**, *40*, 1081–1106; f) L. Heinke, M. Tu, S. Wannapaiboon, R. A. Fischer, C. Wöll, *Microporous Mesoporous Mater.* **2015**, *216*, 200–215.
- [3] a) Y. Cui, B. Chen, G. Qian, *Coord. Chem. Rev.* **2014**, *273–274*, 76–86; b) B. Chen, G. Qian in *Structure and Bonding*, Vol. 157 (Eds.: D. M. P. Mingos), Springer, Heidelberg, **2014**, pp. 1–196; c) L. V. Meyer, F. Schönfeld, K. Müller-Buschbaum, *Chem. Commun.* **2014**, *50*, 8093–8108; d) D. Liu, K. Lu, C. Poon, W. Lin, *Inorg. Chem.* **2014**, *53*, 1916–1924.
- [4] a) Y. Li, S. Zhang, D. Song, *Angew. Chem. Int. Ed.* **2013**, *52*, 710–713; *Angew. Chem.* **2013**, *125*, 738–741; b) J.-J. Wu, Y.-X. Ye, Y.-Y. Qiu, Z.-P. Qiao, M.-L. Cao, B.-H. Ye, *Inorg. Chem.* **2013**, *52*, 6450–6456; c) J. Cui, Z. Lu, Y. Li, Z. Guo, H. Zheng, *Chem. Commun.* **2012**, *48*, 7967–7969.
- [5] a) J. Chen, F.-Y. Yi, H. Yu, S. Jiao, G. Pang, Z.-M. Sun, *Chem. Commun.* **2014**, *50*, 10506–10509; b) M. G. Campbell, D. Sheberla, S. F. Liu, T. M. Swager, M. Dincă, *Angew. Chem.* **2015**, *54*, 4349–4352; *Angew. Chem.* **2015**, *127*, 4423–4426; c) G. Giancane, V. Borovkov, Y. Inoue, L. Valli, *J. Colloid Interface Sci.* **2012**, *385*, 282–284; d) K. Sel, S. Demirci, O. F. Ozturk, N. Aktas, N. Sahiner, *Microelectron. Eng.* **2015**, *136*, 71–76; e) Y. Lin, C. Wang, Y. Pan, L. Xiang, Y. Liu, *Chem. Lett.* **2015**, *44*, 887–889; f) R. Fu, S. Hu, X. Wu, *CrystEngComm* **2011**, *13*, 6007–6009; g) S.-M. Hu, H.-L. Niu, L.-G. Qiu, Y.-P. Yuan, X. Jiang, A.-J. Xie, Y.-H. Shen, J.-F. Zhu, *Inorg. Chem. Commun.* **2012**, *17*, 147–150; h) J.-J. Liu, Y.-F. Guan, M.-J. Lin, C.-C. Huang, W.-X. Dai, *Cryst. Growth Des.* **2015**, *15*, 5040–5046.
- [6] B. Chen, S. Xiang, G. Qian, *Acc. Chem. Res.* **2010**, *43*, 1115–1124.
- [7] a) Y. Takashima, V. M. Martínez, S. Furukawa, M. Kondo, S. Shimomura, H. Uehara, M. Nakahama, K. Sugimoto, S. Kitagawa, *Nat. Commun.* **2011**, *2*, 168; b) Q.-K. Liu, J.-P. Ma, Y.-B. Dong, *J. Am. Chem. Soc.* **2010**, *132*, 7005–7017; c) J. Xiao, Y. Wu, M. Li, B.-Y. Liu, X.-C. Huang, D. Li, *Chem. Eur. J.* **2013**, *19*, 1891–1895; d) G.-L. Liu, Y.-j. Qin, L. Jing, G.-y. Wei, H. Li, *Chem. Commun.* **2013**, *49*, 1699–1701.
- [8] a) Z.-Z. Lu, R. Zhang, Y.-Z. Li, Z.-J. Guo, H.-G. Zheng, *J. Am. Chem. Soc.* **2011**, *133*, 4172–4174; b) Y. Yu, J.-P. Ma, C.-W. Zhao, J. Yang, X.-M. Zhang, Q.-K. Liu, Y.-B. Dong, *Inorg. Chem.* **2015**, *54*, 11590–11592; c) A. Mallick, B. Garai, M. A. Addicoat, P. S. Petkov, T. Heine, R. Banerjee, *Chem. Sci.* **2015**, *6*, 1420–1425; d) X.-L. Qi, R.-B. Lin, Q. Chen, J.-B. Lin, J.-P. Zhang, X.-M. Chen, *Chem. Sci.* **2011**, *2*, 2214–2218; e) N. B. Shustova, B. D. McCarthy, M. Dincă, *J. Am. Chem. Soc.* **2011**, *133*, 20126–20129; f) R. Grunker, V. Bon, A. Heerwig, N. Klein, P. Müller, U. Stoeck, I. A. Baburin, U. Mueller, I. Senkowska, S. Kaskel, *Chem. Eur. J.* **2012**, *18*, 13299–13303; g) M. Zhang, G. Feng, Z. Song, Y.-P. Zhou, H.-Y. Chao, D. Yuan, T. T. Y. Tan, Z. Guo, Z. Hu, B. Z. Tang, B. Liu, D. Zhao, *J. Am. Chem. Soc.* **2014**, *136*, 7241–7244; h) S. A. Sapchenko, D. G. Samsonenko, D. N. Dybtsev, M. S. Melgunov, V. P. Fedina, *Dalton Trans.* **2011**, *40*, 2196–2203; i) S. B. Aliev, D. G. Samsonenko, M. I. Rakhmanova, D. N. Dybtsev, V. P. Fedina, *Cryst. Growth Des.* **2014**, *14*, 4355–4363; j) K. C. Stylianou, R. Heck, S. Y. Chong, J. B. James, T. A. Jones, Y. Z. Khimyak, D. Bradshaw, M. J. Rosseinsky, *J. Am. Chem. Soc.* **2010**, *132*, 4119–4130; k) Q.-K. Liu, J.-P. Ma, Y.-B. Dong, *Chem. Eur. J.* **2009**, *15*, 10364–10368.
- [9] a) B. Chen, Y. Yang, F. Zapata, G. Lin, G. Qian, E. B. Lobkovsky, *Adv. Mater.* **2007**, *19*, 1693–1696; b) F.-Y. Yi, W. Yang, Z.-M. Sun, *J. Mater. Chem.* **2012**, *22*, 23201–23209; c) Z. Hao, X. Song, M. Zhu, X. Meng, S. Zhao, S. Su, W. Yang, S. Song, H. Zhang, *J. Mater. Chem. A* **2013**, *1*, 11043–11050; d) H. Li, W. Shi, K. Zhao, Z. Niu, H. Li, P. Cheng, *Chem. Eur. J.* **2013**, *19*, 3358–3365; e) S. Dang, X. Min, W. Yang, F.-Y. Yi, H. You, Z.-M. Sun, *Chem. Eur. J.* **2013**, *19*, 17172–17179; f) C.-Y. Sun, X.-L. Wang, C. Qin, J.-L. Jin, Z.-M. Su, P. Huang, K.-Z. Shao, *Chem. Eur. J.* **2013**, *19*, 3639–3645; g) X.-Z. Song, S.-Y. Song, S.-N. Zhao, Z.-M. Hao, M. Zhu, X. Meng, L.-L. Wu, H.-J. Zhang, *Adv. Funct. Mater.* **2014**, *24*, 4034–4041; h) H.-N. Wang, S.-Q. Jiang, Q.-Y. Lu, Z.-Y. Zhou, S.-P. Zhuo, G.-G. Shan, Z.-M. Su, *RSC Adv.* **2015**, *5*, 48881–48884.
- [10] a) P. Davydovskaya, A. Ranft, B. V. Lotsch, R. Pohle, *Anal. Chem.* **2014**, *86*, 6948–6968; b) M. M. Wanderley, C. Wang, C.-D. Wu, W. Lin, *J. Am. Chem. Soc.* **2012**, *134*, 9050–9053; c) H. Zhang, D. Chen, H. Ma, P. Cheng, *Chem. Eur. J.* **2015**, *21*, 15854–15859; d) Y. Wang, Y. Lü, W. Zhan, Z. Xie, Q. Kuang, L. Zheng, *J. Mater. Chem. A* **2015**, *3*, 12796–12803; e) R. Li, X. Ren, H. Ma, X. Feng, Z. Lin, X. Li, C. Hu, B. Wang, *J. Mater. Chem. A* **2014**, *2*, 5724–5729; f) Z. Jin, H. He, H. Zhao, T. Borjigin, F. Sun, D. Zhang, G. Zhu, *Dalton Trans.* **2013**, *42*, 13335–13338; g) X. Si, C. Jiao, F. Li, J. Zhang, S. Wang, S. Liu, Z. Li, L. Sun, F. Xu, Z. Gabelicad, C. Schick, *Energy Environ. Sci.* **2011**, *4*, 4522–4527; h) P. J. Calderone, A. M. Plonka, D. Banerjee, Q. A. Nizami, J. B. Parise, *Solid State Sci.* **2013**, *15*, 36–41; i) R. Saha, B. Joarder, A. S. Roy, S. M. Islam, S. Kumar, *Chem. Eur. J.* **2013**, *19*, 16607–16614; j) G. Lu, J. T. Hupp, *J. Am. Chem. Soc.* **2010**, *132*, 7832–7833; k) Z. Dou, J. Yu, H. Xu, Y. Cui, Y. Yang, G. Qian, *Microporous Mesoporous Mater.* **2013**, *179*, 198–204; l) V. Pentylala, P. Davydovskaya, M. Ade, R. Pohle, G. Urbana, *Sens. Actuators B* **2016**, *222*, 904–909; m) J. Hromadka, B. Tokay, S. James, R. P. Tamam, S. Korposh, *Sens. Actuators B* **2015**, *221*, 891–899; n) X. Wan, H. Song, D. Zhao, L. Zhang, Y. Lv, *Sens. Actuators B* **2014**, *201*, 413–419.
- [11] a) J. Zhou, X. Li, L. Yang, S. Yan, M. Wang, D. Cheng, Q. Chen, Y. Dong, P. Liu, W. Cai, C. Zhang, *Anal. Chim. Acta* **2015**, *899*, 57–65; b) S. Dong, G. Suo, N. Li, Z. Chen, L. Peng, Y. Fu, Q. Yang, T. Huang, *Sens. Actuators B* **2016**, *222*, 972–979; c) L. Wen, L. Zhou, B. Zhang, X. Meng, H. Qu, D. Li, *J. Mater. Chem.* **2012**, *22*, 22603–22609; d) Y.-Q. Wang, Q.-H. Tan, H.-T. Liu, W. Sun, Z.-L. Liu, *RSC Adv.* **2015**, *5*, 86614–86619; e) P. Davydovskaya, R. Pohle, A. Tawil, M. Fleischer, *Sens. Actuators B* **2013**, *187*, 142–146; f) P. Wu, J. Wang, Y. Li, C. He, Z. Xie, C. Duan, *Adv. Funct. Mater.* **2011**, *21*, 2788–2794; g) Z.-L. Wu, J. Dong, W.-Y. Ni, B.-W. Zhang, J.-Z. Cui, B. Zhao, *Inorg. Chem.* **2015**, *54*, 5266–5272.
- [12] a) H.-L. Jiang, Y. Tatsu, Z.-H. Lu, Q. Xu, *J. Am. Chem. Soc.* **2010**, *132*, 5586–5587; b) Z. Guo, H. Xu, S. Su, J. Cai, S. Dang, S. Xiang, G. Qian, H. Zhang, M. O’Keeffe, B. Chen, *Chem. Commun.* **2011**, *47*, 5551–5553;

- c) X.-H. Jin, J.-K. Sun, L.-X. Cai, J. Zhang, *Chem. Commun.* **2011**, 47, 2667–2669; d) L. Li, X. Jiao, D. Chen, B. V. Lotsch, C. Li, *Chem. Mater.* **2015**, 27, 7601–7609; e) Y. Lü, W. Zhan, Y. He, Y. Wang, X. Kong, Q. Kuang, Z. Xie, L. Zheng, *ACS Appl. Mater. Interfaces* **2014**, 6, 4186–4195; f) J.-H. Wang, M. Li, D. Li, *Chem. Sci.* **2013**, 4, 1793–1801; g) Z. Guo, X. Song, H. Lei, H. Wang, S. Su, H. Xu, G. Qian, H. Zhang, B. Chen, *Chem. Commun.* **2015**, 51, 376–379; h) X.-G. Liu, H. Wang, B. Chen, Y. Zou, Z.-G. Gu, Z. Zhao, L. Shen, *Chem. Commun.* **2015**, 51, 1677–1680; i) D. Wang, L. Zhang, G. Li, Q. Huo, Y. Liu, *RSC Adv.* **2015**, 5, 18087–18091; j) C. Hou, Y.-L. Bai, X. Bao, L. Xu, R.-G. Lin, S. Zhu, J. Fang, J. Xu, *Dalton Trans.* **2015**, 44, 7770–7773; k) M.-J. Dong, M. Zhao, S. Ou, C. Zou, C.-D. Wu, *Angew. Chem. Int. Ed.* **2014**, 53, 1575–1579; *Angew. Chem.* **2014**, 126, 1601–1605; l) M. Meilikhov, S. Furukawa, K. Hirai, R. A. Fischer, S. Kitagawa, *Angew. Chem. Int. Ed.* **2013**, 52, 341–345; *Angew. Chem.* **2013**, 125, 359–363; m) I.-H. Park, R. Medishetty, H.-H. Lee, C. E. Mulijanto, H. S. Quah, S. S. Lee, J. J. Vittal, *Angew. Chem. Int. Ed.* **2015**, 54, 7313–7317; *Angew. Chem.* **2015**, 127, 7421–7425; n) C. A. Bauer, T. V. Timofeeva, T. B. Settersten, B. D. Patterson, V. H. Liu, B. A. Simmons, M. D. Allendorf, *J. Am. Chem. Soc.* **2007**, 129, 7136–7144; o) S. Xiang, W. Zhou, Z. Zhang, M. A. Green, Y. Liu, B. Chen, *Angew. Chem. Int. Ed.* **2010**, 49, 4615–4618; *Angew. Chem.* **2010**, 122, 4719–4722; p) Y.-L. Hou, H. Xu, R.-R. Cheng, B. Zhao, *Chem. Commun.* **2015**, 51, 6769–6772; q) Z. Yue, Z. Chen, M. Yao, H. Wang, G. Li, *RSC Adv.* **2014**, 4, 33537–33540; r) W.-w. Zhan, Q. Kuang, J.-z. Zhou, X.-j. Kong, Z.-x. Xie, L.-s. Zheng, *J. Am. Chem. Soc.* **2013**, 135, 1926–1933; s) Y. Guo, X. Feng, T. Han, S. Wang, Z. Lin, Y. Dong, B. Wang, *J. Am. Chem. Soc.* **2014**, 136, 15485–15488.
- [13] a) Z. Hu, B. J. Deibert, J. Li, *Chem. Soc. Rev.* **2014**, 43, 5815–5840; b) S. Pramanik, C. Zheng, X. Zhang, T. J. Emge, J. Li, *J. Am. Chem. Soc.* **2011**, 133, 4153–4155; c) S. Pramanik, Z. Hu, X. Zhang, C. Zheng, S. Kelly, J. Li, *Chem. Eur. J.* **2013**, 19, 15964–15971; d) Z. Hu, S. Pramanik, K. Tan, C. Zheng, W. Liu, X. Zhang, Y. J. Chabal, J. Li, *Cryst. Growth Des.* **2013**, 13, 4204–4207.
- [14] F.-Y. Yi, Y. Wang, J.-P. Li, D. Wu, Y.-Q. Lan, Z.-M. Sun, *Mater. Horiz.* **2015**, 2, 245–251.
- [15] a) S. S. Nagarkar, B. Joarder, A. K. Chaudhari, S. Mukherjee, S. K. Ghosh, *Angew. Chem. Int. Ed.* **2013**, 52, 2881–2885; *Angew. Chem.* **2013**, 125, 2953–2957; b) B. Joarder, A. V. Desai, P. Samanta, S. Mukherjee, S. K. Ghosh, *Chem. Eur. J.* **2015**, 21, 965–969; c) J. Ye, X. Wang, R. F. Bogale, L. Zhao, H. Cheng, W. Gong, J. Zhao, G. Ning, *Sens. Actuators B* **2015**, 210, 566–573; d) X.-H. Zhou, L. Li, H.-H. Li, A. Li, T. Yang, W. Huang, *Dalton Trans.* **2013**, 42, 12403–12409; e) J.-D. Xiao, L.-G. Qiu, F. Ke, Y.-P. Yuan, G.-S. Xu, Y.-M. Wang, X. Jiang, *J. Mater. Chem. A* **2013**, 1, 8745–8752; f) S. Barman, J. A. Garg, O. Blacque, K. Venkatesan, H. Berke, *Chem. Commun.* **2012**, 48, 11127–11129; g) A. Li, L. Li, Z. Lin, L. Song, Z.-H. Wang, Q. Chen, T. Yang, X.-H. Zhou, H.-P. Xiao, X.-J. Yin, *New J. Chem.* **2015**, 39, 2289–2295; h) X. Jiang, Y. Liu, P. Wu, L. Wang, Q. Wang, G. Zhu, X.-I. Li, J. Wang, *RSC Adv.* **2014**, 4, 47357–47360; i) C. Zhang, Y. Yan, Q. Pan, L. Sun, H. He, Y. Liu, Z. Liang, J. Li, *Dalton Trans.* **2015**, 44, 13340–13346.
- [16] a) P. Wang, J.-P. Ma, Y.-B. Dong, R.-Q. Huang, *J. Am. Chem. Soc.* **2007**, 129, 10620–10621; b) J. An, C. M. Shade, D. A. Chengelis-Czegán, S. Petoud, N. L. Rosi, *J. Am. Chem. Soc.* **2011**, 133, 1220–1223; c) Y. Zhou, B. Yan, *Inorg. Chem.* **2014**, 53, 3456–3463; d) F.-Y. Yi, J.-P. Li, D. Wu, Z.-M. Sun, *Chem. Eur. J.* **2015**, 21, 11475–11482; e) Y. Gao, X. Zhang, W. Sun, Z. Liu, *Dalton Trans.* **2015**, 44, 1845–1849; f) Y.-Y. Jiang, S.-K. Ren, J.-P. Ma, Q.-K. Liu, Y.-B. Dong, *Chem. Eur. J.* **2009**, 15, 10742–10746; g) Y.-Q. Lan, H.-L. Jiang, S.-L. Li, Q. Xu, *Adv. Mater.* **2011**, 23, 5015–5020; h) L. Chen, K. Tan, Y.-Q. Lan, S.-L. Li, K.-Z. Shao, Z.-M. Su, *Chem. Commun.* **2012**, 48, 5919–5921; i) C.-X. Chen, Q.-K. Liu, J.-P. Ma, Y.-B. Dong, *J. Mater. Chem.* **2012**, 22, 9027–9033; j) J. Cao, Y. Gao, Y. Wang, C. Du, Z. Liu, *Chem. Commun.* **2013**, 49, 6897–6899; k) Y. Wang, J. Yang, Y.-Y. Liu, J.-F. Ma, *Chem. Eur. J.* **2013**, 19, 14591–14599; l) S.-N. Zhao, X.-Z. Song, M. Zhu, X. Meng, L.-L. Wu, J. Feng, S.-Y. Song, H.-J. Zhang, *Chem. Eur. J.* **2015**, 21, 9748–9752.
- [17] a) W. Cho, H. J. Lee, G. Choi, S. Choi, M. Oh, *J. Am. Chem. Soc.* **2014**, 136, 12201–12204; b) B. Chen, L. Wang, Y. Xiao, F. R. Fronczek, M. Xue, Y. Cui, G. Qian, *Angew. Chem. Int. Ed.* **2009**, 48, 500–503; *Angew. Chem.* **2009**, 121, 508–511; c) Y. Xiao, Y. Cui, Q. Zheng, S. Xiang, G. Qian, B. Chen, *Chem. Commun.* **2010**, 46, 5503–5505; d) Z. Wang, H. Liu, S. Wang, Z. Rao, Y. Yang, *Sens. Actuators B* **2015**, 220, 779–787; e) F. Luo, S. R. Batten, *Dalton Trans.* **2010**, 39, 4485–4488; f) P. Zhang, L. Pei, Y. Chen, W. Xu, Q. Lin, J. Wang, J. Wu, Y. Shen, L. Ji, H. Chao, *Chem. Eur. J.* **2013**, 19, 15494–15503; g) C. Liu, B. Yan, *RSC Adv.* **2015**, 5, 101982–101988; h) Y.-W. Li, J.-R. Li, L.-F. Wang, B.-Y. Zhou, Q. Chen, X.-H. Bu, *J. Mater. Chem. A* **2013**, 1, 495–499; i) S. Bhattacharyya, A. Chakraborty, K. Jayaramulu, A. Hazra, T. K. Maji, *Chem. Commun.* **2014**, 50, 13567–13570; j) D. Cai, H. Guo, L. Wen, C. Liu, *CrystEngComm* **2013**, 15, 6702–6708; k) L.-N. Zhang, A.-L. Liu, Y.-X. Liu, J.-X. Shen, C.-X. Du, H.-W. Hou, *Inorg. Chem. Commun.* **2015**, 56, 137–140.
- [18] a) H. Xu, H.-C. Hu, C.-S. Cao, B. Zhao, *Inorg. Chem.* **2015**, 54, 4585–4587; b) Z. Chen, Y. Sun, L. Zhang, D. Sun, F. Liu, Q. Meng, R. Wang, D. Sun, *Chem. Commun.* **2013**, 49, 11557–11559; c) G.-G. Hou, Y. Liu, Q.-K. Liu, J.-P. Ma, Y.-B. Dong, *Chem. Commun.* **2011**, 47, 10731–10733; d) S. Dang, E. Ma, Z.-M. Sun, H. Zhang, *J. Mater. Chem.* **2012**, 22, 16920–16926; e) M. Zheng, H. Tan, Z. Xie, L. Zhang, X. Jing, Z. Sun, *ACS Appl. Mater. Interfaces* **2013**, 5, 1078–1083; f) C.-X. Yang, H.-B. Ren, X.-P. Yan, *Anal. Chem.* **2013**, 85, 7441–7446; g) Q. Tang, S. Liu, Y. Liu, J. Miao, S. Li, L. Zhang, Z. Shi, Z. Zheng, *Inorg. Chem.* **2013**, 52, 2799–2801; h) Z. Xiang, C. Fang, S. Leng, D. Cao, *J. Mater. Chem. A* **2014**, 2, 7662–7665; i) Y. Zhou, H.-H. Chen, B. Yan, *J. Mater. Chem. A* **2014**, 2, 13691–13697; j) X.-Y. Xu, B. Yan, *ACS Appl. Mater. Interfaces* **2015**, 7, 721–729; k) H. Xu, S. Zhou, L. Xiao, H. Wang, S. Li, Q. Yuan, *J. Mater. Chem. C* **2015**, 3, 291–297; l) Y. Wu, G.-P. Yang, X. Zhou, J. Li, Y. Ning, Y.-Y. Wang, *Dalton Trans.* **2015**, 44, 10385–10391; m) Y.-T. Liang, G.-P. Yang, B. Liu, Y.-T. Yan, Z.-P. Xi, Y.-Y. Wang, *Dalton Trans.* **2015**, 44, 13325–13330.
- [19] a) B. Zhao, X.-Y. Chen, P. Cheng, D.-Z. Liao, S.-P. Yan, Z.-H. Jiang, *J. Am. Chem. Soc.* **2004**, 126, 15394–15395; b) G. Xie, Y. Shi, F. Hou, H. Liu, L. Huang, P. Xi, F. Chen, Z. Zeng, *Eur. J. Inorg. Chem.* **2012**, 327–332; c) N. Wei, M.-Y. Zhang, X.-N. Zhang, G.-M. Li, X.-D. Zhang, Z.-B. Han, *Cryst. Growth Des.* **2014**, 14, 3002–3009; d) S. H. Jung, H. Lee, M. L. Seo, J. H. Jung, *Bull. Korean Chem. Soc.* **2013**, 34, 1583–1585.
- [20] a) J.-N. Hao, B. Yan, *Chem. Commun.* **2015**, 51, 7737–7740; b) C. Liu, B. Yan, *J. Colloid Interface Sci.* **2015**, 459, 206–211; c) L.-r. Yang, S. Song, H.-m. Zhang, W. Zhang, Z.-w. Bu, T.-g. Ren, *Synth. Met.* **2011**, 161, 2230–2240; d) N. Wei, Y.-R. Zhang, Z.-B. Han, *CrystEngComm* **2013**, 15, 8883–8886.
- [21] a) H. Tan, B. Liu, Y. Chen, *ACS Nano* **2012**, 6, 10505–10511; b) J. Jia, F. Xu, Z. Long, X. Hou, M. J. Sepaniak, *Chem. Commun.* **2013**, 49, 4670–4672; c) Y.-M. Zhu, C.-H. Zeng, T.-S. Chu, H.-M. Wang, Y.-Y. Yang, Y.-X. Tong, C.-Y. Su, W.-T. Wong, *J. Mater. Chem. A* **2013**, 1, 11312–11319; d) P. Wu, Y. Liu, Y. Liu, J. Wang, Y. Li, W. Liu, J. Wang, *Inorg. Chem.* **2015**, 54, 11046–11048.
- [22] a) J.-N. Hao, B. Yan, *J. Mater. Chem. A* **2014**, 2, 18018–18025; b) W. Liu, T. Jiao, Y. Li, Q. Liu, M. Tan, H. Wang, L. Wang, *J. Am. Chem. Soc.* **2004**, 126, 2280–2281; c) L. Zhang, Y. Jian, J. Wang, C. He, X. Li, T. Liu, C. Duan, *Dalton Trans.* **2012**, 41, 10153–10155.
- [23] a) L. Cui, J. Wu, J. Li, H. Ju, *Anal. Chem.* **2015**, 87, 10635–10641; b) Y. Wang, Y. Wu, J. Xie, X. Hu, *Sens. Actuators B* **2013**, 177, 1161–1166; c) W.-G. Lu, L. Jiang, X.-L. Feng, T.-B. Lu, *Inorg. Chem.* **2009**, 48, 6997–6999; d) S.-R. Zhang, J. Li, D.-Y. Du, J.-S. Qin, S.-L. Li, W.-W. He, Z.-M. Su, Y.-Q. Lan, *J. Mater. Chem. A* **2015**, 3, 23426–23434; e) B. Zhao, X.-Y. Chen, Z. Chen, W. Shi, P. Cheng, S.-P. Yan, D.-Z. Liao, *Chem. Commun.* **2009**, 3113–3115; f) X.-Q. Zhao, B. Zhao, W. Shi, P. Cheng, *CrystEngComm* **2009**, 11, 1261–1269; g) J.-x. Ma, X.-f. Huang, X.-q. Song, W.-s. Liu, *Chem. Eur. J.* **2013**, 19, 3590–3595; h) M. L. Carboni, Z. Lin, C. W. Abney, T. Zhang, W. Lin, *Chem. Eur. J.* **2014**, 20, 14965–14970; i) D. Maity, T. Govindaraju, *Eur. J. Inorg. Chem.* **2011**, 5479–5485; j) L.-H. Cao, F. Shi, W.-M. Zhang, S.-Q. Zang, T. C. W. Mak, *Chem. Eur. J.* **2015**, 21, 15705–15712; k) A. Shahat, H. M. A. Hassan, H. M. E. Azzazy, *Anal. Chim. Acta* **2013**, 793, 90–98.
- [24] a) B. Chen, L. Wang, F. Zapata, G. Qian, E. B. Lobkovsky, *J. Am. Chem. Soc.* **2008**, 130, 6718–6719; b) J.-M. Zhou, W. Shi, N. Xu, P. Cheng, *Inorg. Chem.* **2013**, 52, 8082–8090; c) K.-L. Wong, G.-L. Law, Y.-Y. Yang, W.-T. Wong, *Adv. Mater.* **2006**, 18, 1051–1054; d) H. Liu, H. Wang, T. Chu, M. Yu, Y. Yang, *J. Mater. Chem. C* **2014**, 2, 8683–8690; e) P.-F. Shi, H.-C. Hu, Z.-Y. Zhang, G. Xiong, B. Zhao, *Chem. Commun.* **2015**, 51, 3985–3988; f) C.-F. Chow, M. H. W. Lam, W.-Y. Wong, *Inorg. Chem.* **2004**, 43, 8387–8393; g) H.-B. Xu, J.-G. Deng, L.-Y. Zhang, Z.-N. Chen, *Cryst. Growth Des.* **2013**, 13, 849–857; h) J.-M. Zhou, W. Shi, H.-M. Li, H. Li, P. Cheng, *J. Phys. Chem. C* **2014**, 118, 416–426; i) Y. Wang, L. Cheng, Z.-Y. Liu, X.-G. Wang, B. Ding, L. Yin, B.-B. Zhou, M.-S. Li, J.-X. Wang, X.-J. Zhao, *Chem. Eur. J.* **2015**, 21, 14171–14178; j) X. Li, H. Xu, F. Kong, R. Wang, *Angew.*

- Chem. Int. Ed.* **2013**, *52*, 13769–13773; *Angew. Chem.* **2013**, *125*, 14014–14018.
- [25] a) J.-P. Ma, Y. Yu, Y.-B. Dong, *Chem. Commun.* **2012**, *48*, 2946–2948; b) B. Manna, B. Joarder, A. V. Desai, A. Karmakar, S. K. Ghosh, *Chem. Eur. J.* **2014**, *20*, 12399–12404; c) Y. Qiu, H. Deng, J. Mou, S. Yang, M. Zeller, S. R. Batten, H. Wu, J. Li, *Chem. Commun.* **2009**, 5415–5417; d) H. Xu, Y. Xiao, X. Rao, Z. Dou, W. Li, Y. Cui, Z. Wang, G. Qian, *J. Alloys Compd.* **2011**, *509*, 2552–2554; e) Y.-Q. Chen, G.-R. Li, Z. Chang, Y.-K. Qu, Y.-H. Zhang, X.-H. Bu, *Chem. Sci.* **2013**, *4*, 3678–3682; f) J. Wang, J. Wu, Y. Chen, H. Wang, Y. Li, W. Liu, H. Tian, T. Zhang, J. Xu, Y. Tang, *Dalton Trans.* **2012**, *41*, 12936–12941; g) Q.-B. Bo, H.-T. Zhang, H.-Y. Wang, J.-L. Miao, Z.-W. Zhang, *Chem. Eur. J.* **2014**, *20*, 3712–3723; h) L. J. Charbonnière, R. Ziessel, M. Montalti, L. Prodi, N. Zaccheroni, C. Boehme, G. Wipff, *J. Am. Chem. Soc.* **2002**, *124*, 7779–7788; i) Q.-K. Liu, J.-P. Ma, Y.-B. Dong, *Chem. Commun.* **2011**, *47*, 7185–7187; j) C. Hou, J. Peng, Q. Xu, Z. Ji, X. Hu, *RSC Adv.* **2012**, *2*, 12696–12698.
- [26] a) Z. Xie, L. Ma, K. E. deKrafft, A. Jin, W. Lin, *J. Am. Chem. Soc.* **2010**, *132*, 922–923; b) Y.-T. Chen, C.-Y. Lin, G.-H. Lee, M.-L. Ho, *CrystEngComm* **2015**, *17*, 2129–2140; c) Y.-N. Gong, T.-B. Lu, *Chem. Commun.* **2013**, *49*, 7711–7713; d) S. M. Barrett, C. Wang, W. Lin, *J. Mater. Chem.* **2012**, *22*, 10329–10334; e) M.-L. Ho, Y.-A. Chen, T.-C. Chen, P.-J. Chang, Y.-P. Yu, K.-Y. Cheng, C.-H. Shih, G.-H. Lee, H.-S. Sheu, *Dalton Trans.* **2012**, *41*, 2592–2600; f) J. J. Gassensmith, J. Y. Kim, J. M. Holcroft, O. K. Farha, J. F. Stoddart, J. T. Hupp, N. C. Jeong, *J. Am. Chem. Soc.* **2014**, *136*, 8277–8282; g) L. E. Kreno, J. T. Hupp, R. P. V. Duyne, *Anal. Chem.* **2010**, *82*, 8042–8046.
- [27] a) Y. Ma, H. Su, X. Kuang, X. Li, T. Zhang, B. Tang, *Anal. Chem.* **2014**, *86*, 11459–11463; b) H. Li, X. Feng, Y. Guo, D. Chen, R. Li, X. Ren, X. Jiang, Y. Dong, B. Wang, *Sci. Rep.* **2014**, *4*, 4366; c) S. S. Nagarkar, A. V. Desai, S. K. Ghosh, *Chem. Eur. J.* **2015**, *21*, 9994–9997; d) J. Cui, Y.-L. Wong, M. Zeller, A. D. Hunter, Z. Xu, *Angew. Chem. Int. Ed.* **2014**, *53*, 14438–14442; *Angew. Chem.* **2014**, *126*, 14666–14670; e) A. V. Desai, P. Samanta, B. Manna, S. K. Ghosh, *Chem. Commun.* **2015**, *51*, 6111–6114; f) P. Wu, J. Wang, C. He, X. Zhang, Y. Wang, T. Liu, C. Duan, *Adv. Funct. Mater.* **2012**, *22*, 1698–1703; g) N. B. Shustova, A. F. Cozzolino, S. Reineke, M. Baldo, M. Dincă, *J. Am. Chem. Soc.* **2013**, *135*, 13326–13329; h) X.-P. Zhou, Z. Xu, J. He, M. Zeller, A. D. Hunter, R. Clérac, C. Mathonière, S. S.-Y. Chui, C.-M. Che, *Inorg. Chem.* **2010**, *49*, 10191–10198; i) N. L. A. Travlou, K. Singh, E. Rodríguez-Castellón, T. J. Bandosz, *J. Mater. Chem. A* **2015**, *3*, 11417–11429; j) E. X. Chen, H. Yang, J. Zhang, *Inorg. Chem.* **2014**, *53*, 5411–5413; k) S. Achmann, G. Hagen, J. Kita, I. M. Malkowsky, C. Kiener, R. Moos, *Sensors* **2009**, *9*, 1574–1589; l) G. Nickler, I. Senkowska, S. Kaskel, *Chem. Commun.* **2015**, *51*, 2280–2282.
- [28] a) W. J. Rieter, K. M. L. Taylor, W. Lin, *J. Am. Chem. Soc.* **2007**, *129*, 9852–9853; b) H. Xu, X. Rao, J. Gao, J. Yu, Z. Wang, Z. Dou, Y. Cui, Y. Yang, B. Chen, G. Qian, *Chem. Commun.* **2012**, *48*, 7377–7379; c) L. Chen, H. Zheng, X. Zhu, Z. Lin, L. Guo, B. Qiu, G. Chen, Z.-N. Chen, *Analyst* **2013**, *138*, 3490–3493; d) H.-T. Zhang, J.-W. Zhang, G. Huang, Z.-Y. Du, H.-L. Jiang, *Chem. Commun.* **2014**, *50*, 12069–12072; e) P. Ling, J. Lei, L. Zhang, H. Ju, *Anal. Chem.* **2015**, *87*, 3957–3963; f) L. Zhang, J. Lei, F. Ma, P. Ling, J. Liu, H. Ju, *Chem. Commun.* **2015**, *51*, 10831–10834; g) W. Lu, X. Qin, A. M. Asiri, A. O. Al-Youbi, X. Sun, *Analyst* **2013**, *138*, 429–433; h) H. Hosseini, H. Ahmar, A. Dehghani, A. Bagheri, A. Tadjarodi, A. R. Fakhari, *Biosens. Bioelectron.* **2013**, *42*, 426–429.
- [29] a) T. Lee, H. L. Lee, M. H. Tsai, S.-L. Cheng, S.-W. Lee, J.-C. Hu, L.-T. Chen, *Biosens. Bioelectron.* **2013**, *43*, 56–62; b) P. Ling, J. Lei, H. Ju, *Biosens. Bioelectron.* **2015**, *71*, 373–379; c) X. Wang, X. Wang, Y. Wang, Z. Guo, *Chem. Commun.* **2011**, *47*, 8127–8129; d) X. Zhu, H. Zheng, X. Wei, Z. Lin, L. Guo, B. Qiu, G. Chen, *Chem. Commun.* **2013**, *49*, 1276–1278; e) F. Luo, Y. Lin, L. Zheng, X. Lin, Y. Chi, *ACS Appl. Mater. Interfaces* **2015**, *7*, 11322–11329; f) S. Keskin, S. Kizilel, *Ind. Eng. Chem. Res.* **2011**, *50*, 1799–1812; g) E. Zhou, Y. Zhang, Y. Li, X. He, *Electroanalysis* **2014**, *26*, 2526–2533.
- [30] a) Y. Yu, X.-M. Zhang, J.-P. Ma, Q.-K. Liu, P. Wang, Y.-B. Dong, *Chem. Commun.* **2014**, *50*, 1444–1446; b) Y. Yu, J.-P. Ma, Y.-B. Dong, *CrystEngComm* **2012**, *14*, 7157–7160; c) J. Liu, F. Sun, F. Zhang, Z. Wang, R. Zhang, C. Wang, S. Qiu, *J. Mater. Chem.* **2011**, *21*, 3775–3778; d) A. L. Robinson, V. Stavila, T. R. Zeitler, M. I. White, S. M. Thornberg, J. A. Great-house, M. D. Allendorf, *Anal. Chem.* **2012**, *84*, 7043–7051; e) Y. Zhang, Y. Chen, Y. Zhang, H. Cong, B. Fu, S. Wen, S. Ruan, *J. Nanopart. Res.* **2013**, *15*, 2014; f) A. Douvali, A. C. Tsipis, S. V. Eliseeva, S. Petoud, G. S. Papaefstathiou, C. D. Malliakas, I. Papadas, G. S. Armatas, I. Margiolaki, M. G. Kanatzidis, T. Lazarides, M. J. Manos, *Angew. Chem. Int. Ed.* **2015**, *54*, 1651–1656; *Angew. Chem.* **2015**, *127*, 1671–1676; g) W.-H. Zhu, Z.-M. Wang, S. Gao, *Inorg. Chem.* **2007**, *46*, 1337–1342; h) A. Weiss, N. Reimer, N. Stock, M. Tiemann, T. Wagner, *Phys. Chem. Chem. Phys.* **2015**, *17*, 21634–21642; i) M.-H. Zeng, Y.-X. Tan, Y.-P. He, Z. Yin, Q. Chen, M. Kurmoo, *Inorg. Chem.* **2013**, *52*, 2353–2360; j) C. Sapsanis, H. Omran, V. Chernikova, O. Shekhah, Y. Belmabkhout, U. Buttner, M. Eddaoudi, K. N. Salama, *Sensors* **2015**, *15*, 18153–18166; k) J. Ferrando-Soria, H. Khajavi, P. Serra-Crespo, J. Gascon, F. Kapteijn, M. Julve, F. Lloret, J. Pasán, C. Ruiz-Pérez, Y. Journaux, E. Pardo, *Adv. Mater.* **2012**, *24*, 5625–5629.
- [31] a) B. V. Harbuzaru, A. Corma, F. Rey, J. L. Jordá, D. Ananias, L. D. Carlos, J. Rocha, *Angew. Chem. Int. Ed.* **2009**, *48*, 6476–6479; *Angew. Chem.* **2009**, *121*, 6598–6601; b) H.-L. Jiang, D. Feng, K. Wang, Z.-Y. Gu, Z. Wei, Y.-P. Chen, H.-C. Zhou, *J. Am. Chem. Soc.* **2013**, *135*, 13934–13938; c) B. J. Deibert, J. Li, *Chem. Commun.* **2014**, *50*, 9636–9639; d) J. Aguilera-Sigalat, D. Bradshaw, *Chem. Commun.* **2014**, *50*, 4711–4713; e) C. He, K. Lu, W. Lin, *J. Am. Chem. Soc.* **2014**, *136*, 12253–12256; f) M. Zan, J. Li, S. Luo, Z. Ge, *Chem. Commun.* **2014**, *50*, 7824–7827; g) Y. Lu, B. Yan, *Chem. Commun.* **2014**, *50*, 13323–13326; h) Y.-H. Han, C.-B. Tian, Q.-H. Li, S.-W. Du, *J. Mater. Chem. C* **2014**, *2*, 8065–8070; i) Q. Meng, X. Xin, L. Zhang, F. Dai, R. Wang, D. Sun, *J. Mater. Chem. A* **2015**, *3*, 24016–24021; j) H.-Y. Li, Y.-L. Wei, X.-Y. Dong, S.-Q. Zang, T. C. W. Mak, *Chem. Mater.* **2015**, *27*, 1327–1331.
- [32] Y. Cui, F. Zhu, B. Chen, G. Qian, *Chem. Commun.* **2015**, *51*, 7420–7431.
- [33] a) Y. Cui, H. Xu, Y. Yue, Z. Guo, J. Yu, Z. Chen, J. Gao, Y. Yang, G. Qian, B. Chen, *J. Am. Chem. Soc.* **2012**, *134*, 3979–3982; b) X. Rao, T. Song, J. Gao, Y. Cui, Y. Yang, C. Wu, B. Chen, G. Qian, *J. Am. Chem. Soc.* **2013**, *135*, 15559–15564; c) Y. Cui, W. Zou, R. Song, J. Yu, W. Zhang, Y. Yang, G. Qian, *Chem. Commun.* **2014**, *50*, 719–721; d) C. D. S. Brites, P. P. Lima, N. J. O. Silva, A. Millán, V. S. Amaral, F. Palacio, L. D. Carlos, *J. Lumin.* **2013**, *133*, 230–232; e) J. Yu, L. Sun, H. Peng, M. I. J. Stich, *J. Mater. Chem.* **2010**, *20*, 6975–6981; f) P. Falcaro, S. Furukawa, *Angew. Chem. Int. Ed.* **2012**, *51*, 8431–8433; *Angew. Chem.* **2012**, *124*, 8557–8559; g) S. M. F. Vilela, D. Ananias, A. C. Gomes, A. A. Valente, L. D. Carlos, J. A. S. Cavaleiro, J. Rocha, J. P. C. Tomé, F. A. A. Paz, *J. Mater. Chem.* **2012**, *22*, 18354–18371; h) A. Cadiau, C. D. S. Brites, P. M. F. J. Costa, R. A. S. Ferreira, J. Rocha, L. D. Carlos, *ACS Nano* **2013**, *7*, 7213–7218; i) K. Miyata, Y. Konno, T. Nakanishi, A. Kobayashi, M. Kato, K. Fushimi, Y. Hasegawa, *Angew. Chem. Int. Ed.* **2013**, *52*, 6413–6416; *Angew. Chem.* **2013**, *125*, 6541–6544; j) R. F. D’Vries, S. Álvarez-García, N. Snejko, L. E. Bausá, E. Gutiérrez-Puebla, A. d. Andrés, M. Ángeles Monge, *J. Mater. Chem. C* **2013**, *1*, 6316–6324; k) Y. Zhou, B. Yan, *Nanoscale* **2015**, *7*, 4063–4069; l) Y. Zhou, B. Yan, *J. Mater. Chem. C* **2015**, *3*, 9353–9358.
- [34] a) L.-N. Sun, J. Yu, H. Peng, J. Z. Zhang, L.-Y. Shi, O. S. Wolfbeis, *J. Phys. Chem. C* **2010**, *114*, 12642–12648; b) H. Peng, M. I. J. Stich, J. Yu, L.-n. Sun, L. H. Fischer, O. S. Wolfbeis, *Adv. Mater.* **2010**, *22*, 716–719; c) Y. Cui, R. Song, J. Yu, M. Liu, Z. Wang, C. Wu, Y. Yang, Z. Wang, B. Chen, G. Qian, *Adv. Mater.* **2015**, *27*, 1420–1425; d) D. Ma, B. Li, X. Zhou, Q. Zhou, K. Liu, G. Zeng, G. Li, Z. Shi, S. Feng, *Chem. Commun.* **2013**, *49*, 8964–8966; e) D. Sun, L. Zhang, H. Lu, S. Feng, D. Sun, *Dalton Trans.* **2013**, *42*, 3528–3532.

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