

“Turn-on” Fluorescence Sensing and Discriminative Detection of Aliphatic Amines Using a 5-Fold-Interpenetrated Coordination Polymer

Prabu Mani,[†] Anupam Anand Ojha,[†] Vennapusa Sivaranjana Reddy,[†] and Sukhendu Mandal^{*,†}

[†]School of Chemistry, Indian Institute of Science Education and Research Thiruvananthapuram, Thiruvananthapuram, Kerala, India 695016

S Supporting Information

ABSTRACT: A 5-fold-interpenetrated zinc-based coordination polymer can discriminately detect aliphatic amines through a fluorescence “turn-on” method. This compound can sense aliphatic amines in the solid state, solution state, and vapor phase. Theoretical calculations revealed that the ground-state dipole moment of the corresponding amines guides the order of enhancement.

The sensing of amines is important because they are hazardous wastes and lead to heavy environmental pollution.^{1–3} Amines are almost ubiquitous analytes in our daily life for the determination of food freshness, disease state, etc. Recently, luminescence-based sensing methods have gained considerable attention because of their ease of manipulation, high sensitivity, and real-time monitoring with rapid response time.^{4,5} The sensitive detection of individual amines has been previously reported, but the discriminative detection of amines within a larger family is rare.^{6,7} Molecular recognition of amines is challenging because of its extensive range of molecular shapes,⁸ sizes,^{9,10} and electronic properties.¹¹ A chemical sensor can detect an analyte through change in the luminescence, conductivity, and sometimes color, etc.¹² However, analytes like explosives and hazardous chemicals need to be detected in very low concentrations to avoid the danger inherent in them. Most of the analyte sensing carried out in the past has been through fluorescence quenching, that is, “turn off” in nature.^{13–15} An example of fluorescence intensity enhancement (“turn on”) is rare and essential for the device application.¹⁶ The predesigned synthesis of a “turn-on” sensor is a challenge because several factors interfere with the fluorescence process. To our knowledge, very few sensors are reported in which amines are detected through fluorescence enhancement or a “turn-on” process.¹⁶

Metal–organic frameworks (MOFs) or coordination polymers (CPs) can act as sensors because of their quick, reversible, and recyclable sensing ability.^{12,17–19} MOFs or CPs are inorganic–organic hybrid crystalline materials with diverse architectures and variable pore sizes constructed by the linking of metal ions or metal clusters and organic ligands.^{20–25} The diverse pore topologies and functional sites may be responsible for molecular-level interactions between the framework and analytes.^{12,17} These types of interactions may also be responsible for specific and selective sensing of particular analytes. It is interesting to adopt an effective strategy to synthesize MOFs or CPs for the discriminative detection of amines in which the

interactions between an electron-deficient ligand and electron-rich amines can perturb the photoluminescence properties. However, synthesizing an electron-deficient MOF or CP with a predesigned architecture is challenging because of its high reactivity during the synthesis. There are reports where MOFs or CPs have been used for the detection of organic amines.^{7,15} Recently, Banerjee et al. synthesized an electron-deficient magnesium-based photochromic porous MOF that can discriminately sense organic amines in the solid state.⁷ Here, we synthesized a new three-dimensional CP, [Zn(PA)(BPE)] [1; PA = pamoic acid and BPE = 1,2-bis(4-pyridyl)ethane]. This compound can discriminately detect aliphatic amines in the solid state, solution state, and vapor phase. Interactions between amines and compound 1 lead to “turn-on” fluorescence. Theoretical calculations showed that the ground-state dipole moment of the corresponding amines directs the order of fluorescence enhancement.

Compound 1 was synthesized by the solvothermal reaction of Zn(NO₃)₂·6H₂O, PA, and BPE at 120 °C for 72 h [see the Supporting Information (SI) for the detailed synthesis]. Compound 1 crystallizes in space group Cc (see the SI). The zinc metal ions adopt a distorted tetrahedral geometry. The Zn–O/N bond lengths are in the range of 1.92–2.06 Å. The zinc ions are linked with the PA ligand to form a one-dimensional chain (Figure 1a). Each chain is linked with four other chains through the BPE ligand to form a three-dimensional structure (Figure 1b). Topological analysis using TOPOS software identified that the structure has 5-fold interpenetration with a uninodal 4-c net (Figure 1c).²⁶ The overall structure has a dia net topology with the Schläfli point symbol {6⁶}, which can be presented as the Schläfli symbol {6².6².6².6².6²} (see the SI).²⁶

The powder X-ray diffraction (PXRD) pattern of the as-synthesized material matched well with the simulated pattern (Figure S1a), indicating a crystalline phase purity. Compound 1 retained its PXRD pattern after the addition of analyte molecules (such as various solvents and amines), indicating retention of the structural integrity after treatment with analyte molecules (Figure S1b–d). Fourier transform infrared analysis shows the presence of organic moieties (Figure S2). Thermogravimetric analysis shows that compound 1 is stable up to 350 °C in a N₂ atmosphere (Figure S3). The structural features show that compound 1 is a 5-fold-interpenetrated structure with negligible

Received: March 30, 2017

Published: May 30, 2017



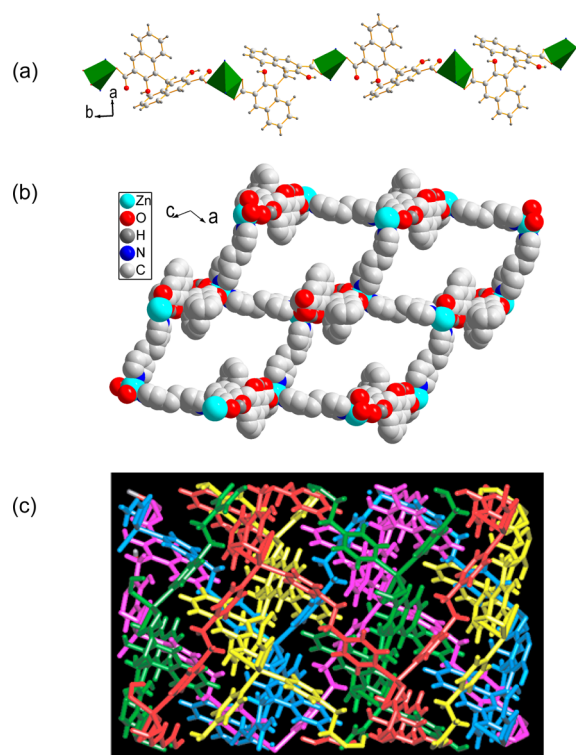


Figure 1. (a) One-dimensional chain formed through the connectivity of a metal ion and the PA ligand in 1. (b) Three-dimensional connectivity. (c) 5-fold interpenetration.

void space. N_2 adsorption analysis also indicated the presence of $16 \text{ cm}^2 \text{ g}^{-1}$ available surface area within this compound (Figure S4). According to this, analyte molecules may not enter inside the pores but instead interact on the surface.

Both ligands PA and BPE display strong absorption bands at 300–450 nm in the solution phase (Figure S5). A blue shift for PA and a red shift for BPE are observed for the as-synthesized compound 1. Solid- and solution-state luminescence of compound 1 as well as the free ligands PA and BPE has been investigated upon excitation at 369 nm at room temperature (Figures S6a,b). In solution, compound 1 exhibits a broad emission band with λ_{max} at 507 nm.

Interestingly, this compound can sense only aliphatic amines with an increase in the fluorescence intensity. Electron-rich organic amines can transfer electrons to compound 1, resulting in enhancement of the fluorescence with a change in color. When compound 1 is treated with various organic amines, it shows a prominent color change for aliphatic amines compared to aromatic amines (Figure S7) and no color change for other analytes (Figures 2a,b). To explore the sensing ability of compound 1, we performed fluorescence titration with the incremental addition of analytes to a fixed amount of compound 1. A wide range of amines like ethylenediamine (EDA), *n*-butylamine (n-BA), diisopropylamine (DIPA), *N,N,N',N'*-tetramethylethylenediamine (TMEDA), triethylamine (TEA), aniline, etc., were used to test the sensing ability of compound 1. The results imply that compound 1 can discriminately detect aliphatic amines through “turn-on” fluorescence intensity changes (Figures 2c and S8). The use of as-synthesized MOFs or CPs is rare for sensing applications in the solid state. Here, a solid-state sensing experiment was carried out by immersing 10 mg of compound 1 in different 0.1 M aliphatic amines [in *N,N*-dimethylformamide (DMF)] for a time period of 24 h. The

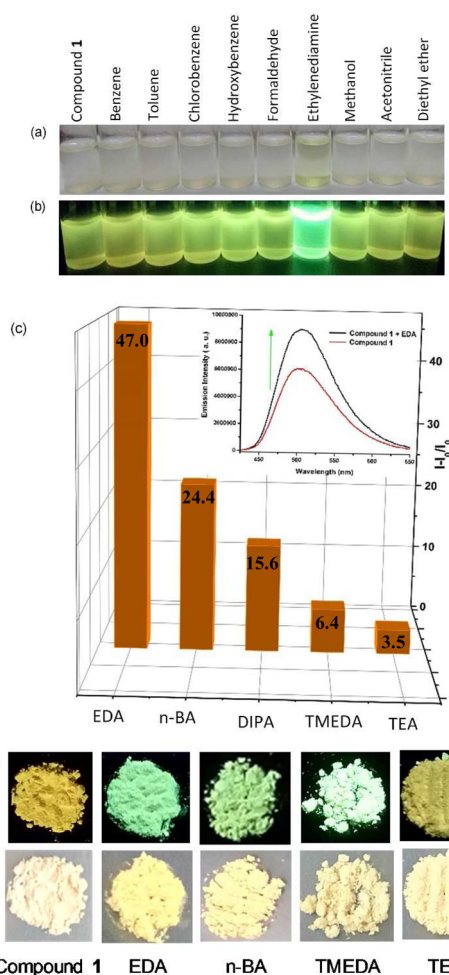


Figure 2. Photograph for the selective detection of amine over other organic molecules under (a) visible and (b) UV light. (c) Bar diagram representing the fluorescence enhancement efficiency of compound 1 in different amines (0.03 M dimethyl sulfoxide). Inset: Photoluminescence spectra of compound 1 before and after amine addition. Photographs showing the color change of compound 1 (solid state) in different amines (0.1 M DMF) under (d) UV and (e) visible light.

observed color change in visible light is more prominent under UV light (Figures 2d,e).

In the present case, we also tested the vapor-phase sensing of amine molecules. Upon exposure to amine vapors, the photoluminescence property of compound 1 was enhanced. This showed that compound 1 can also be used for the real-time detection of aliphatic amines in the vapor phase (Figure S9). The detection limit of compound 1 (in solution) toward EDA was found to be on the order of $166 \mu\text{M}$. Literature reports show that the present compound is one of the rare examples which can discriminately detect aliphatic amines in all the phases of matter through fluorescence enhancement (“turn-on”) process (Table S4). On the basis of our assumption, enhancement of the fluorescence intensity should follow the basicity of the corresponding amines. However, the enhancement order does not follow the basicity order. The order of fluorescence enhancement is EDA (47.0%) > n-BA (24.4%) > DIPA (15.6%) > TMEDA (6.4%) > TEA (3.5%) (Figures 2c and S10).

To underscore the mechanism for this “turn-on” fluorescent sensing, we carried out theoretical calculations using density functional theory (DFT) methods (see the SI). We optimized the asymmetric unit of compound 1 as a representative fragment

for theoretical studies (Table S5 and Figure S11). The theoretical UV–vis spectrum has a maximum absorption band centered at 365 nm in the gas phase, which is in agreement with the experimental value of 369 nm (Figure S12).

Because the theoretically calculated UV–vis spectrum and optimized geometric parameters are in excellent accordance with the experimental values (Table S5), the representative fragment can be treated as a valid representation of compound **1**. Earlier studies suggest that fluorescence quenching occurs when the energies of the lowest unoccupied molecular orbital (LUMO) of the analytes lie between the valence (VB) and conduction (CB) bands of the MOF or CP.^{12,17,27} This happens because electrons in the CB of MOF or CP are transferred to the LUMO of analytes. A contrasting phenomenon is observed when the fluorescence intensity is enhanced.²⁸ It is seen that the PA ligand largely contributes to the highest occupied molecular orbital (HOMO), while the BPE ligand forms the LUMO. In our case, theoretical calculations indicate that the LUMO of electron-rich amines lies higher in energy than the CB of compound **1** (Figure 3a). Upon photoexcitation of the analytes, more electrons in the LUMO of amines would populate the CB of compound **1**. This therefore results in fluorescence enhancement.

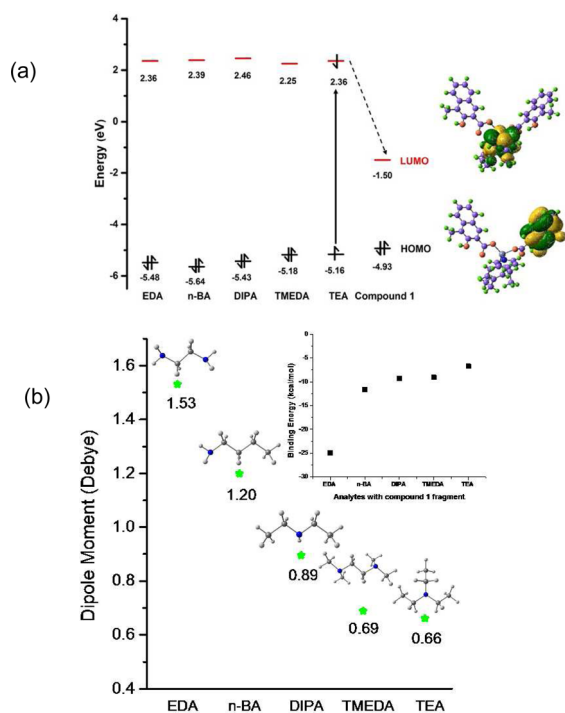


Figure 3. (a) Schematic representation of the fluorescence enhancement mechanism in the gas phase. (b) Dipole moments of the amines. Inset: Variation of the binding energy of the analytes with compound **1**.

Therefore, a lower LUMO energy of the analyte indicates higher fluorescence enhancement. The fluorescence enhancement toward EDA, n-BA, and DIPA is in good agreement with the experimental findings. However, the enhancement of the other two analytes deviates from the trend in their LUMO energies. This trend in the fluorescence enhancement may be attributed to dipole–dipole interactions between the amines and compound **1**.¹⁹

Dipole–dipole interactions between compound **1** and the analytes are important to explain the discriminative enhancement behavior of compound **1** toward different amines. As a

consequence of the pore-size limitations, the analytes can only interact with compound **1** at the surface. Subsequently, dipole–dipole interactions lead to excited-state electron transfer from the electron-rich analytes to compound **1**. The trend in the dipole moment follows the order EDA > n-BA > DIPA > TMEDA > TEA (Figure 3b). EDA possesses the maximum dipole moment and therefore leads to maximum fluorescence enhancement among the analytes. Theoretical findings are in complete agreement with the experimentally observed fluorescence enhancement. To understand the nature of the interaction between the analytes and compound **1**, calculations are performed at the hybrid metaGGA DFT of the M06-2X level²⁸ with a 6-31G basis set. First of all, individual molecules were optimized using the earlier mentioned level of theory (Figure S13). Binding energies of -25.01 , -11.68 , -9.36 , -9.10 , and -6.38 kcal mol⁻¹ are found for EDA, n-BA, DIPA, TMEDA, and TEA with the LUMO of the compound, respectively (Table S7 and Figure 3b,inset). This trend in the binding energy is in accordance with the trend in the fluorescent enhancement (Figure 2c).

In conclusion, we synthesized a 5-fold-interpenetrated three-dimensional zinc-metal-based CP. To our knowledge, this is a rare example where this compound can discriminately detect aliphatic amine in all phases of matter through the “turn-on” fluorescence process. Theoretical calculations predict that dipole–dipole interactions between the surface of the as-synthesized CP (where the LUMO is localized) and different aliphatic amines are responsible for the discriminative detection.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b00787.

Synthesis, crystal structure determination, several characterization figures, UV–vis and photoluminescence spectra, computational calculations and related figures (PDF)

Accession Codes

CCDC 1517779 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sukhendu@iisertvm.ac.in (S.M.).

ORCID

Vennapusa Sivarajana Reddy: 0000-0002-8252-9586

Sukhendu Mandal: 0000-0002-4725-8418

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We acknowledge the Science and Engineering Research Board, Government of India, for funding through Grant SB/S1/IC-14/2013. We acknowledge Dr. Asha K. S., Dr. K. Nagarajan, and Reena K. Sen for useful scientific discussions.

REFERENCES

- (1) Merchant, Z. M.; Cheng, S. G. G. In *Characterization of Foods, Emerging Methods*; Gaonkar, A. G., Ed.; Elsevier Science: New York, 1995; Chapter 15.
- (2) Ajayakumar, M. R.; Mukhopadhyay, P. Naphthalene-bis-hydrazimide: radical anions and ICT as new bimodal probes for differential sensing of a library of amines. *Chem. Commun.* **2009**, 25, 3702–3704.
- (3) Bao, B.; Yuwen, L.; Zheng, X.; Weng, L.; Zhu, X.; Zhan, X.; Wang, L. A fluorescent conjugated polymer for trace detection of diamines and biogenic polyamines. *J. Mater. Chem.* **2010**, 20, 9628–9634.
- (4) (a) Hulanicki, A.; Glab, S.; Ingman, F. Chemical Sensors Definitions and Classification. *Pure Appl. Chem.* **1991**, 63, 1247–1250. (b) Hinoue, T.; Miyata, M.; Hisaki, I.; Tohnai, N. Guest-Responsive Fluorescence of Inclusion Crystals with n-Stacked Supramolecular Beads. *Angew. Chem., Int. Ed.* **2012**, 51, 155–158.
- (5) Stetter, J. R.; Penrose, W. R.; Yao, S. Sensors, Chemical Sensors, Electrochemical Sensors, and ECS. *J. Electrochem. Soc.* **2003**, 150, S11–S16.
- (6) Liu, J. J.; Shan, Y. B.; Fan, C. R.; Lin, M. J.; Huang, C. C.; Dai, W. X. Encapsulating Naphthalene in an Electron-Deficient MOF to Enhance Fluorescence for Organic Amines Sensing. *Inorg. Chem.* **2016**, 55, 3680–3684.
- (7) Mallick, A.; Garai, B.; Addicoat, M. A.; Petkov, P.; St.; Heine, T.; Banerjee, R. Solid state organic amine detection in a photochromic porous metal organic framework. *Chem. Sci.* **2015**, 6, 1420–1425.
- (8) Mertz, E.; Zimmerman, S. C. Cross-Linked Dendrimer Hosts Containing Reporter Groups for Amine Guests. *J. Am. Chem. Soc.* **2003**, 125, 3424–3425.
- (9) Greene, N. T.; Morgan, S. L.; Shimizu, K. D. Molecularly imprinted polymer sensor arrays. *Chem. Commun.* **2004**, 1172–1173.
- (10) Comes, M.; Marcos, M. D.; Martínez-Mañez, R.; Sancenon, F.; Soto, J.; Villaescusa, L. A.; Amoros, P.; Beltran, D. Chromogenic Discrimination of Primary Aliphatic Amines in Water with Functionalized Mesoporous Silica. *Adv. Mater.* **2004**, 16, 1783–1786.
- (11) Mohr, G. J. Chromo- and Fluororeactands: Indicators for Detection of Neutral Analytes by Using Reversible Covalent-Bond Chemistry. *Chem. - Eur. J.* **2004**, 10, 1082–1090.
- (12) Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; Van Duyne, R. P.; Hupp, J. T. Metal–Organic Framework Materials as Chemical Sensors. *Chem. Rev.* **2012**, 112, 1105–1125.
- (13) Che, Y.; Zang, L. Enhanced fluorescence sensing of amine vapor based on ultrathin nanofibers. *Chem. Commun.* **2009**, 34, 5106–5108.
- (14) Takashima, Y.; Martínez, V. M.; Furukawa, S.; Kondo, M.; Shimomura, S.; Uehara, H.; Nakahama, M.; Sugimoto, K.; Kitagawa, S. Molecular decoding using luminescence from an entangled porous framework. *Nat. Commun.* **2011**, 2, 168.
- (15) Liu, J. J.; Shan, Y. B.; Fan, C. R.; Lin, M. J.; Huang, C. C.; Dai, W. X. Encapsulating Naphthalene in an Electron-Deficient MOF to Enhance Fluorescence for Organic Amines Sensing. *Inorg. Chem.* **2016**, 55, 3680–3684.
- (16) Kumpf, J.; Freudenberg, J.; Fletcher, K.; Dreuw, A.; Bunz, U. H. F. Detection of Amines with Extended Distyrylbenzenes by Strip Assays. *J. Org. Chem.* **2014**, 79, 6634–6645.
- (17) Pramanik, S.; Zheng, C.; Zhang, X.; Emge, T. J.; Li, J. New Microporous Metal–Organic Framework Demonstrating Unique Selectivity for Detection of High Explosives and Aromatic Compounds. *J. Am. Chem. Soc.* **2011**, 133, 4153–4155.
- (18) (a) Gole, B.; Bar, A. K.; Mukherjee, P. S. Fluorescent metal–organic framework for selective sensing of nitroaromatic explosives. *Chem. Commun.* **2011**, 47, 12137–12139. (b) Wang, J. H.; Li, M.; Li, D. A dynamic, luminescent and entangled MOF as a qualitative sensor for volatile organic solvents and a quantitative monitor for acetonitrile vapour. *Chem. Sci.* **2013**, 4, 1793–1801.
- (19) Asha, K. S.; Bhattacharyya, K.; Mandal, S. Discriminative detection of nitro aromatic explosives by a luminescent metal–organic framework. *J. Mater. Chem. C* **2014**, 2, 10073–10081.
- (20) Yaghi, O. M.; Li, H.; Eddaoudi, M.; O’Keeffe, M. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* **1999**, 402, 276–279.
- (21) Deng, H.; Grunder, S.; Cordova, K. E.; Valente, C.; Furukawa, H.; Hmadeh, M.; Gandara, F.; Whalley, A. C.; Liu, Z.; Asahina, S.; Kazumori, H.; O’Keeffe, M.; Terasaki, O.; Stoddart, J. F.; Yaghi, O. M. Large-Pore Apertures in a Series of Metal-Organic Frameworks. *Science* **2012**, 336, 1018–1023.
- (22) Huang, R. W.; Wei, Y. S.; Dong, X. Y.; Wu, X. H.; Du, C. X.; Zang, S. Q.; Mak, T. C. W. Hypersensitive dual-function luminescence switching of a silver-chalcogenolate cluster-based metal–organic framework. *Nat. Chem.* **2017**, DOI: 10.1038/nchem.2718.
- (23) Bloch, W. M.; Burgun, A.; Coghlan, C. J.; Lee, R.; Coote, M. L.; Doonan, C. J.; Sumbly, C. J. Capturing snapshots of post-synthetic metallation chemistry in metal–organic frameworks. *Nat. Chem.* **2014**, 6, 906–912.
- (24) Van Humbeck, J. F.; McDonald, T. M.; Jing, X.; Wiers, B. M.; Zhu, G.; Long, J. R. Ammonia Capture in Porous Organic Polymers Densely Functionalized with Brønsted Acid Groups. *J. Am. Chem. Soc.* **2014**, 136, 2432–2440.
- (25) Deria, P.; Bury, W.; Hupp, J. T.; Farha, O. K. Versatile functionalization of the NU-1000 platform by solvent-assisted ligand incorporation. *Chem. Commun.* **2014**, 50, 1965–1968.
- (26) Blatov, A. V.; Proserpio, D. M. Topological relations between three-periodic nets. II. Binodal nets. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2009**, 65, 202–212.
- (27) Gole, B.; Bar, A.; Mukherjee, P. Modification of Extended Open Frameworks with Fluorescent Tags for Sensing Explosives: Competition between Size Selectivity and Electron Deficiency. *Chem. - Eur. J.* **2014**, 20, 2276–2291.
- (28) Hu, Z.; Deibert, B.; Li, J. Luminescent metal–organic frameworks for chemical sensing and explosive detection. *Chem. Soc. Rev.* **2014**, 43, 5815–5840.