IJRAR.ORG E-ISSN: 2348-1269, P-ISSN: 2349-5138

INTERNATIONAL JOURNAL OF RESEARCH AND ANALYTICAL REVIEWS (IJRAR) | IJRAR.ORG

An International Open Access, Peer-reviewed, Refereed Journal

Versatile Roles of Metal–Organic Complexes: From Electrochemical Sensing to Gas Storage and Separation

Biplab Biswas

Department of Chemistry, Hooghly Mohsin College, Chinsurah 712101, India

Abstract

The diverse range of structural and electronic characteristics of metal-organic complexes (MOCs) are extremely significant in a variety of scientific applications. Because of their easy synthetic tunability and selective interaction with analytes, Schiff base metal complexes are being studied extensively as optical and electrochemical sensors for the detection of pollutants, poisons, and illicit narcotics. Again due to the vast surface area, tunable chemical functionality, and adjustable pore size, porous MOCs exhibit better functionalities in gas storage, especially for hydrogen, methane, and carbon dioxide. MOCs' structural flexibility and chemical diversity present viable paths to affordable, scalable, and effective technologies for addressing the world's energy and environmental demands. This paper discusses two significant areas—sensor application, gas storage and separation—where MOCs have been demonstrated to have a significant impact.

Keywords: Schiff base metal complexes, Sensors, Metal-organic frameworks (MOFs), Gas storage

1. Introduction

Metal–organic complexes (MOCs) are a broad family of materials with exceptional structural tunability and functional characteristics, especially those that include transition metals coordinated to organic ligands like Schiff bases or carboxylates. These compounds are attractive candidates for applications in sensing, catalysis, magnetic materials, gas storage, optoelectronics, and medicine because of their unique characteristics, which include their rich coordination chemistry, varied oxidation states, and simplicity of synthetic modification [1–3]. Numerous functional materials, such as coordination polymers (CPs) and metal–organic frameworks (MOFs), with specialized features for certain tasks have been developed in recent decades as a result of the rich chemistry of transition metals combined with the versatility of organic ligands [4,5].

Chemical sensing is arguably the most explored application of MOCs. The development of sensors based on MOCs has been prompted by the growing need for sensitive, selective, and economical sensors to detect harmful ions, environmental pollutants, illegal narcotics, and biomedical analytes. Schiff bases along with their metal complexes have found special usage as active materials in electrochemical and optical sensors due to their inherent chelating properties and adaptability in structural modification [6]. Their use in electroanalytical detection systems is favored because they can function as electrode recognition elements [7,8]. These complexes have been integrated onto chemically modified electrodes, enabling very selective trace detection of target analytes [9]. Their multidisciplinary significance has been

highlighted by more recent research that has demonstrated their potential in drug detection, environmental monitoring, and forensic science [10].

MOCs, especially MOFs, have demonstrated exceptional potential in the fields of gas storage and thus separation, in addition to other fields of application. Multidentate bridging organic linkers ligate metal ions or clusters to form MOFs, which are crystalline materials with very porous frameworks and large interior surface areas [11]. The efficient storage and selective adsorption of industrially important gases such as carbon dioxide (CO_2), methane (CH_4), and hydrogen (H_2) are made possible by this porosity in conjunction with tunable pore environments [12]. For instance, under various circumstances, materials like MOF-177, HKUST-1, and MOF-74 have demonstrated significant gas uptake capabilities [13–15].

For the development of clean energy technologies, hydrogen storage is of great importance. As weak van der Waals interactions between H_2 molecules and the framework, to achieve practical storage capacity, MOFs must be constructed by incorporating functional sites or modifying pore diameters [16]. Similarly, MOFs are being investigated more thoroughly in relation to methane storage, where compounds like $_{mono}$HKUST-1 and Ni-MOF-74 have been discovered to be advantageous for natural gas vehicles [17,18].

Furthermore, attempts to reduce greenhouse gas emissions depend on the capture and hence separation of CO_2 from industrial flue gas. Remarkable CO_2 selectivity and adsorption have been reported for MOFs with amine-functionalized pores or, with open metal sites, offering viable paths toward carbon capture technologies [19,20]. MOFs are potential next-generation materials for environmentally friendly and sustainable energy because of their structural flexibility and functionalization ability, which enable fine-tuning of gas sorption behavior.

In this review, we focus on two key applications of metal–organic complexes: (1) chemical sensing, particularly by electrochemical and voltammetric approaches with Schiff base complexes, and (2) H_2, CH_4 gas storage as well as CO_2 capture and separation using metal–organic frameworks. These two domains demonstrate how logical design and functionality of MOCs may address global issues in health, security, and sustainable energy.

2 Applications of Metal-organic complexes

Transition metal-organic complexes are easily produced at low cost. These compounds exhibit a variety of structural and electronic properties that enable their use in a wide range of research areas. Here we discuss their use as sensors and gas storage materials.

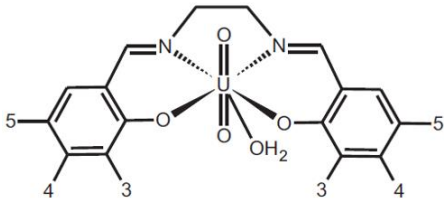
2.1 Sensors

Threats to the environment and public health have increased as a result of industrial and agricultural practices that release pollutants. Crime networks deal in a wide range of substances, that include heroin, cocaine, methamphetamine, and cannabis. Thus, the demand for sensitive and specific detection of pollutants (*e.g.*, metal ions and toxins) is high, especially in applications related to health, environment, and forensic fields. Presently, different techniques, *e.g.*, flame atomic absorption spectroscopy, inductively coupled plasma mass spectrometry, inductively coupled plasma optical emission spectroscopy, X-ray fluorescence spectrometry, and stripping voltammetry are used to detect metal ions [21]. However, the majority of these techniques have low sensitivity, are costly, and time-consuming. Various optical chemosensors have been investigated for the identification of metal ions to get over the previously mentioned drawbacks of the said methods [22]. In view of this, Schiff base-based structures work exceptionally well to identify metal ions.

Scientists working in various areas of electroanalysis have devised electrochemical sensors using different compounds over the past decades. Inexpensive and facile synthesis, along with the wide variety of electronic and structural features of Schiff bases and their complexes have drawn significant interest in modifying electrodes chemically by using them [23]. For this, the resultant electrodes have been utilized as probes and/or sensors in numerous fields. The consequence

of all this interest is the development of sensors at low prices [24-27]. Specifically, the differing structural and electrical characteristics of Schiff bases and their transition metal complexes enable them to interact distinctly with the analyte, hence enhancing the selectivity and sensitivity of the sensor [24-28]. Different kinds of donor atoms in Schiff bases and associated transition metal complexes can alter electrode responsiveness. The application of chemical modifiers in the logical design of an efficient sensor will be governed by these donor atoms [27,29,30]. In fact, Schiff bases and their transition metal complexes are widely used chemical modifiers in a variety of electroanalytical detection systems because they can function as electrode recognition elements [27,28]. Electroanalytical measurements such as Cyclic Voltammetry (CV), Square Wave Voltammetry (SWV), Differential Pulse Voltammetry (DPV), Linear Sweep Voltammetry (LSV), and potentiometric measurements were employed.

In the forensic field, de Oliveira et al. [31] explored the potential usage of $[UO_2(X\text{-MeO-salen})(H_2O)].H_2O$, where X denotes the position (3, 4 or 5) of methoxy group on the aromatic ring, containing salen-type Schiff bases (**Figure 1**) as chemical modifiers of the electrode. Among these complexes, $[UO_2(3\text{-MeO-salen})(H_2O)].H_2O$ was found to be more effective in identifying cocaine in the presence of interfering compounds like procaine and lidocaine using voltammetry.



$[UO_2(X\text{-MeO-salen})(H_2O)]$
X= 3, 4 or 5

Figure 1: Complexes of uranyl Schiff base used as chemical modifiers to identify the illicit drugs mentioned above. X= methoxy substitution at 3, 4 or 5

Hence, these complexes can be utilized in preliminary tests to identify cocaine in apprehended drug samples. Ribeiro et al. [32] explored a chemically modified screen-printed electrode (gold, carbon, and platinum), by employing methanolic solutions of the Schiff base complex $[UO_2(4\text{-MeO-salen})(H_2O)].H_2O$, to identify cocaine, by voltammetric analysis, in the presence of MDMA (methylenedioxy-methylamphetamine) and morphine. This technique provided a low-cost and fast procedure to identify cocaine at trace levels.

Cobalt Salophen complex (**Figure 2(a1)**) was employed as a CPE (Carbon Paste Electrode) chemical modifier to investigate the commercially available medicine cephalexin and cefazolin by cyclic

Complex	Z
1	H
2	Cl
3	NO_2

Complex	X	Y	Z	A
1	H	H	H	ClO_4^-
2	H	OCH_3	CH_3	ClO_4^-
3	H	Cl	CH_3	ClO_4^-
4	H	H	CH_3	ClO_4^- or CH_3COO^-

Figure 2: Structure of substituted salophen complexes of (a) Co(II) and (b) Co(III).

Voltammetry [33]. Penicillamine, was identified in trace quantities ($1x10^{-7}$ mol L^{-1}) by Differential Pulse Voltammetry (DPV) with [Co(Salophen)] as a CPE chemically modifier in acetate and phosphate buffers [9]. Antithyroid agent methimazole was detected using a sensor containing of a CPE chemically modified with different substituted Co(III)(Salophen)]ClO_4 (**Figure 2(b)**) complexes [34].

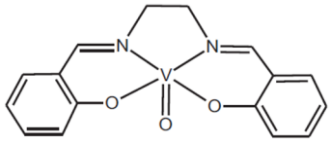


Figure 3: Structure of vanadyl-salen complex, [VO(Salen)]

[VO(Salen)] complex as a chemical modifier for CPE was utilized as a sensor (w/w; **Figure 3**) to detect dipyrone analgesic by LSV and CV [35]. A low-cost and fast sensor utilizing a Schiff base octahedral complex of zinc(II) (**Figure 4**) as a chemical modifier for CPE detected cephalosporin and cefotaxime antibiotics with high sensitivity [36].

Singh and Singh utilized two newly synthesized Zn(II) macrocyclic complex, in which the best results were obtained when a zinc complex of 6,7:14,15-Bzo_2-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N_2-1,5-O_2 and 6,7:14,15-Bzo_2-10,11-(4-methylbenzene)-[15]-6,14-diene-9,12-dimethylacrylate-9,12-N_2-1,5-O_2 (**Figure 5(a)**) were used as chemical modifier for PVC membrane electrode to detect thiocyanate in saliva and urine [37]. In 2008, Singh and Mehtab have shown that the two Cadmium(II) complexes of Schiff base ligand N,N'-bis(salicylidene)-1,4-diaminobutane and N,N

-bis(salicylidene)-3,4-diaminotoluene (**Figure 5(b))** can detect iodide in river water, seawater, and mouthwash [38].

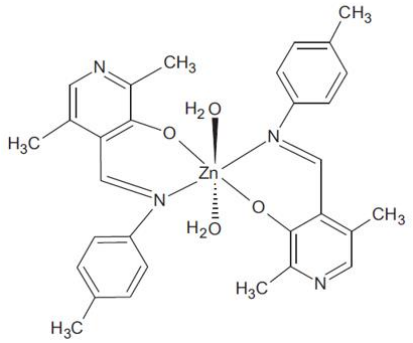


Figure 4: Structures of Zn(II)-Schiff base complex, [$Zn(Hbppyr)_2.2H_2O$]

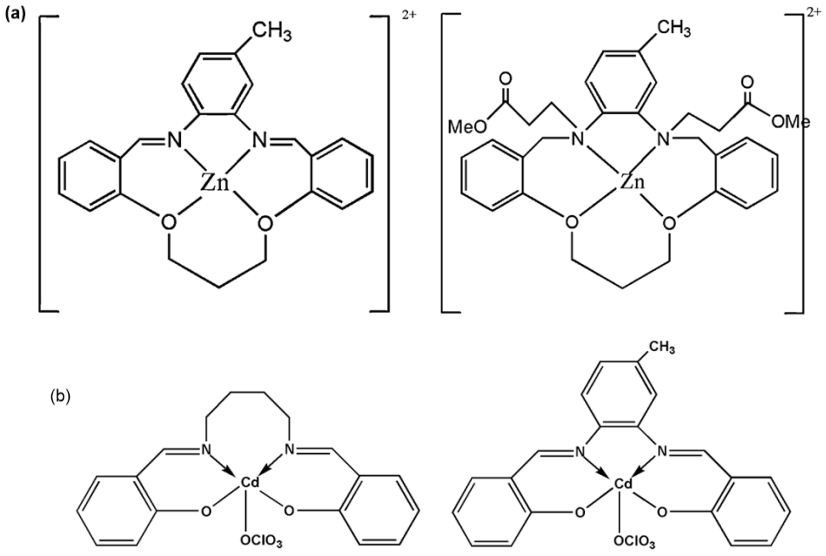


Figure 5: Structures of Schiff base complexes of Zn(II) and Cd(III) used as electrode chemical modifiers.

Dey et al. have reported a water-soluble metal-organic complex {[Cu(n-BuM)(2,2'-bipyridine)(H_2O)]$_2$[Cu_2(n-BuM)$_2$(2,2'-bipyridine)$_2$].6H_2O} [where n-$BuMH_2$ = n-butylmalonic acid], an inorganic co-crystal (ICC) of one monomeric and one dimeric units of Cu(II) (**Figure 6**) exhibited selective As^{3+} sensing capability in aqueous medium in the concentration of pico-molar range in comparison to other metal ions [39].

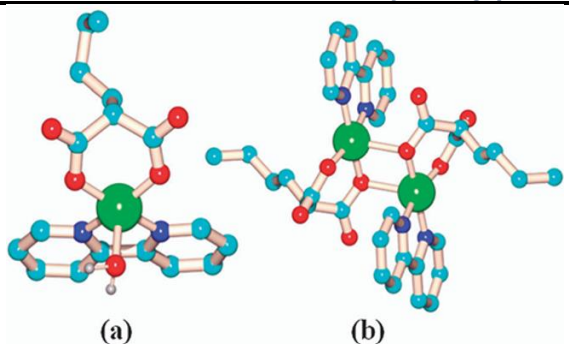


Figure 6: Molecular diagram of inorganic co-crystal of Cu(II), {[Cu(n-BuM)(2,2'-bipyridine)(H_2O)]$_2$[Cu_2(n-BuM)$_2$(2,2'-bipyridine)$_2$].6H_2O} [where n-BuMH_2 = n-butylmalonic acid] (C = cyan, N = blue, O = red, Cu = green)

Jiang and coworkers synthesized a new multifunctional **Zn-TCPP** MOF utilizing newly prepared tetraphenylpyrazine-based tetracarboxylic ligand 2,3,5,6-tetrakis(4-carboxyphenyl)pyrazine (H_4TCPP). The MOF was used as a sensor to detect Fe^{3+} ions and picric acid (PA) [40].

2.2 Gas Storage and Separation

Porous materials play a significant role in capturing and hence storing and separating gases, due to their inherent voids or channels, via non covalent interactions. Among MOCs metal-organic frameworks (MOFs) are one of the types of metal-organic complexes which are porous in nature. Thus, these are excellent choices for gas separation and storage. The high surface area and high pore volume determine the quantity of gas that can be stored in the structure. While nearly any gas can be stored inside a MOF structure methane, CO_2, and H_2 are the most significant. Weak van der Waals interactions are the main acting force which operates for hydrogen, the cleanest energy source, storage. Thus, pure MOF structures are not sufficient to meet the necessary hydrogen storage criteria. To resolve this issue, active metal sites or benzene rings could be included within the MOF structure. At low temperatures, the requisite storage limitations can be achieved with these MOF derivatives.

Another valuable energy source is methane (natural gas), when contrasted with fossil fuels. Natural gas, comprised primarily of methane, generates far less carbon dioxide and other harmful gases than traditional fossil fuels, but it is not as clean as hydrogen energy. Methane can be transported more conveniently, its working pressure can be lowered, and its fuel density may be increased by storing it in a suitable medium. In comparison to porous carbon structures or zeolites, MOFs show remarkable methane storage capabilities.

In addition to storing pure gases, MOFs can be employed for selective gas separation and adsorption from a mixture. In reality, most of the gases in the industry are mixtures, and thus, selective adsorption is crucial in practical applications. To lower CO_2 emissions, it's important to capture carbon dioxide from the flue gas after combustion and also from the precombustion of hydrogen and methane. Open metal sites and the addition of amine functionalities to the MOF structure enhance the selective CO_2 adsorption from a mixture of gases. The flexible structure of MOFs offers great potential for applications in gas separation. MOFs act as a molecular filter and only adsorb the gas molecules of specific sizes i.e., if the pore diameters match the size of the gas molecules. Different functional groups in the void of MOF also enhance the binding energy.

2.2.1 Hydrogen storage:

MOFs' large surface area and tunable structure can offer potent H_2 adsorption sites [41,42]. The hydrogen molecules get attached inside the pore by the weak van der Walls force, which decreases with distance, hence pore size similar to that of molecular hydrogen molecule enhances this interaction. Although larger pore size can accommodate higher amount oh hydrogen molecule under high pressure [43,44]. $Cu_3(BTC)_2$ (BTC = benzene-1,3,5-tricarboxylic acid) is a prime

example of this high pressure effect [45]. Correlation between the surface area and the hydrogen uptake is provided by MOF-177, MOF-74, HKUST-1 at 77K [46]. Ni_2(m-dobdc) have been found to have highest H_2 uptake capcity of 11.0 g/L to 23.0 g/L in the pressure range of 5-100 bar and temperature swing between 298-198K [47].

2.2.2 Methane Storage:

The MOF following which exploration of the field of adsorption started is $[Co_2(4,4'\text{-bpy})_3(NO_3)_4]$ [48]. The adsorption depends on the electrostatic as well as van der Waals interaction between CH_4 and MOF [45]. M-MOF-74 (M=Mg, Mn, Co, Ni, Zn) have been found to exhibit high CH_4 uptake capacity [49]. Among these Ni-MOF-74 have extraordinarily high methane uptake capacity probably due to high polarising capacity of Ni^{2+}. The monolithic framework $_{mono}$HKUST-1 shows methane capacity of 259 cm^3 cm^{-3} at 65 bar [50].

2.2.3 CO_2 capture and separation:

Efficient and selective CO_2 capture has been the major interest for scientists for decades. IRMOF-1, MOF-177, MOF-2, MOF-74, HKUST-1 etc. adsorb CO_2. Among these MOF-177 exhibit highest CO_2 uptake capacity of 33.5 mmol/g at room temperature at 35 bar [51]. Mg-MOF-74 also exhibits high CO2 adsorption capacity [52]. SIFSIX-3-M (SiF^{6-}; M = Cu, Ni, Zn) MOFs also shows remarkable CO_2 uptake capacity. Under atmospheric conditions SIFSIX-3-Cu absorbs highest quantity of CO_2, 1.24 mmol/g [53].

3. Conclusion

Metal–organic complexes offer a very versatile platform for innovation in environmental and energy applications. Significant progress has been made in the development of sensitive, selective sensors and high-capacity gas storage materials due to their adjustable characteristics, flexible architectures, and functional ligand frameworks. It has been demonstrated that Schiff base transition metal complexes are economical and efficient chemical modifiers for electroanalytical sensing instruments that can detect illicit drugs, heavy metals, and antibiotics. However, because of their porosity and adjustable framework chemistry, MOFs continue to show promise for the storage of gases like hydrogen and methane as well as the capture and separation of gases like CO_2. Future developments in green chemistry, sustainable technologies, and public health could result from further rational design and functionalization of these complexes.

References:

1. Kaim, W.; Schwederski, B., Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, **2013**, Wiley.
2. Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M., Advanced Inorganic Chemistry, **1999**, 6th ed. Wiley.
3. Ghosh, S. K.; Functional Metal–Organic Frameworks: Gas Storage, Separation and Catalysis, **2014**, Wiley-VCH.
4. Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J., Nature, **2003**, 423, 705–714.
5. Férey, G., Chemical Society Reviews, **2008**, 37, 191–214.
6. Oiye, É. N.; Ribeiro, M. F. M.; Katayama, J. M. T.; Tadini, M. C.; Balbino, M. A., Eleotério, I. C.; Magalhães, J.; Castro, A. S.; Silva, R. S. M.; da Cruz Júnior, J. W.; Dockal, E. R.. Critical Reviews in Analytical Chemistry, **2019**, 49, 488-509.
7. Fatibello-Filho, O.; Dockal, E. R.; Marcolino-Junior, L. H., Anal. Lett., **2007**, 40, 1825–1852.
8. Al Zoubi, W.; Al Mohanna, N., Spectrochim. Acta A, **2014**, 132, 854–870.
9. Shahrokhian, S.; Souri, A.; Khajehsharifi, H.; J. Electroanal. Chem., **2004**, 565, 95–101.
10. Dincă, M.; Long, J. R., Angew. Chem. Int. Ed., **2008**, 47, 6766–6779.
11. Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D. -W., Chemical Reviews, **2012**, 112, 782–835.
12. Mason, J. A.; Veenstra, M.; Long, J. R.; Chemical Science, **2014**, 5, 32–51.
13. Férey, G.; et al., Science, **2005**, 309, 2040–2042.

14. Furukawa, H.; Ko, N.; Go, Y. B.; et al., Science, **2010**, 329, 424–428.

15. Bae, Y. S.; Snurr, R. Q., Angew. Chem. Int. Ed., **2011**, 50, 11586–11596.

16. He, Y.; Chen, F.; Li, B.; Qian, G.; Zhou, W.; Chen, B., Coord. Chem. Rev., **2018**, 373, 167–198.

17. Tian, T.; Zeng, Z.; Vulpe, D.; Casco, M. E.; Divitini, G.; Midgley, P. A.; Silvestre-Albero, J.; Tan, J. C.; Moghadam, P. Z.; Fairen-Jimenez, D., Nat. Mater., **2018**, 17, 174–179.

18. Mason, J. A.; Veenstra, M.; Long, J. R., Chem. Sci., **2014**, 5, 32–51.

19. Sumida, K.; Rogow, D. L.; Mason, J. A.; McDonald, T. M.; Bloch. E.D.; Herm, Z. R.; Bae, T-H.; Long, J. R., Chemical Reviews, **2012**, 112, 724–781.

20. Kizzie, A. C.; Wong-Foy, A. G.; Matzger, A. J., Langmuir, **2011**, 27, 6368–6373.

21. Bansod, B.; Kumar, T.; Thakur, R.; Rana, S.; Singh, I., Biosens. Bioelectron., **2017**, 94, 443-455.

22. De Silva, A. P.; McCaughan, B.; McKinney, B. O.; Querol, M., Dalton Trans., **2003**, 10. 1902-1913.

23. Oiye, É. N.; Ribeiro, M. F. M., Katayama, J. M. T.; Tadini, M. C.; Balbino, M. A.; Eleotério, I. C.; Magalhães, J.; Castro, A. S.; Silva, R. S. M.; da Cruz Júnior, J. W.; Dockal, E. R., Critical Reviews in Analytical Chemistry, **2019**, 49(6), 488-509.

24. Tozzo, E.; Romera, S.; dos Santos, M. P.; Muraro, M.; de A. Santos, R. H.; Liao, L. M.; Vizotto, L.; Dockal, E. R., J. Mol. Struct., **2008**, 876, 110–120.

25. Masoudi, M.; Behzad, M.; Arab, A.; Tarahhomi, A.; Rudbari, H. A.; Bruno, G., J. Mol. Struct., **2016**, 1122, 123–133.

26. Cozzi, P. G., Chem. Soc. Rev., **2004**, 33, 410–421.

27. Fatibello-Filho, O.; Dockal, E. R.; Marcolino-Junior, L. H., Anal. Lett., **2007**, 40, 1825–1852.

28. Al Zoubi, W.; Al Mohanna, N., Spectrochim. Acta A, **2014**, 132, 854–870.

29. El-Sherif, A. A.; Aljahdali, M. S., J. Coordin. Chem., **2013**, 66, 3423–3468.

30. Priya, N. P.; Arunachalam, S.; Manimaran, A.; Muthupriya, D.; Jayabalakrishnan, C., Spectrochim. Acta A: Mol. Biomol. Spectrosc., **2009**, 72, 670–676.

31. de Oliveira, L. S.; Balbino, M. A.; de Menezes, M. M. T.; Dockal, E. R.; de Oliveira, M. F., Microchem. J., **2013**, 110, 374–378.

32. Ribeiro, M. F. M.; Jr. da Cruz, J. W.; Dockal, E. R.; McCord, B. R.; de Oliveira, M. F., Electroanalysis, **2016**, 28, 320–326.

33. Jamasbi, E. S.; Rouhollahi, A.; Shahrokhian, S.; Haghgoo, S.; Aghajani, S., Talanta, **2007**, 71, 1669–1674.

34. Shahrokhian, S.; Ghalkhani, M., Electroanalysis, **2008**, 20, 1061–1066.

35. Teixeira, M. F. S.; Marcolino-Junior, L. H.; Fatibello-Filho, O.; Dockal, E. R.; Cavalheiro, E. T. G.; J. Braz. Chem. Soc., **2004**, 15, 803–808.

36. Nigam, P.; Mohan, S.; Kundu, S.; Prakash, R., Talanta, **2009**, 77, 1426–1431.

37. Singh, P.; Singh, A. K., Anal. Bioanal. Chem., **2011**, 400, 2261–2269.

38. Singh, A. K.; Mehtab, S., Talanta, **2008**, 74, 806–814.

39. Dey, B.; Saha, R.; Mukherjee, P., Chem. Commun., **2013**, 49, 7064-7066.

40. Jiang, Y.; Sun, L.; Du, J.; Liu, Y.; Shi, H.; Liang, Z.; Li, J., Cryst. Growth Des., **2017**, 17, 4, 2090–2096.

41. Li, H.; Wang, K.; Sun, Y.; Lollar, C. T.; Li, J.; Zhou, H. C., Mater. Today, **2018**, 21, 108–121.

42. Li, H.; Li, L.; Lin, R.-B.; Zhou, W.; Zhang, Z.; Xiang, S.; Chen, B., EnergyChem, **2019**, 1, 100006.

43. He, Y.; Chen, F.; Li, B.; Qian, G.; Zhou, W.; Chen, B., Coord. Chem.Rev., **2018**, 373, 167–198.

44. Dresselhaus, M. S.; Williams, K. A.; Eklund, P. C.; MRS Bull., **1999**,24, 45–50.

45. Yang, H.; Orefuwa, S.; Goudy, A., Microporous Mesoporous Mater., **2011**, 143, 37–45.

46. Wong-Foy, A. G.; Matzger, A. J.; Yaghi, O. M., J. Am. Chem. Soc., **2006**, 128, 3494–3495.

47. Kapelewski, M. T.; Runčevski, T.; Tarver, J. D.; Jiang, H. Z. H.; Hurst, K. E.; Parilla, P. A.; Ayala, A.; Gennett, T.; Fitzgerald, S. A.; Brown, C. M.; Long, J. R., Chem. Mater., **2018**, 30, 8179–8189.

48. Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S., Angew. Chemie - Int. Ed., **1997**, 36, 1725–1727.

49. Mason, J. A.; Veenstra, M.; Long, J. R., Chem. Sci., **2014**, 5, 32–51.

50. Tian, T.; Zeng, Z.; Vulpe, D.; Casco, M. E.; Divitini, G.; Midgley, P. A.; Silvestre-Albero, J.; Tan, J. C.; Moghadam, P. Z.; Fairen-Jimenez, D., Nat. Mater., **2018**, 17, 174–179.

51. Millward, A. R.; Yaghi, O. M., J. Am. Chem. Soc., **2005**, 127, 17998–17999.

52. Yazaydin, A. Ö.; Snurr, R. Q.; Park, T. H.; Koh, K.; Liu, J.; LeVan, M. D.; Benin, A. I.; Jakubczak, P.; Lanuza, M.; Galloway, D. B.; Low, J. J.; Willis, R. R., J. Am. Chem. Soc., **2009**, 131, 18198–18199.

53. Shekhah, O.; Belmabkhout, Y.; Chen, Z.; Guillerm, V.; Cairns, A.; Adil, K.; Eddaoudi, M., Nat. Commun., **2014**, 5, 4228.