

1 **An Ongoing Futuristic Career of Metal-Organic Frameworks and**
2 **Ionic Liquids, A Magical Gateway to Capture CO₂; A Critical**
3 **Review.**

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35 **Abstract**

36 Carbon capture and storage (CCS) technologies are the “knight in shining armor” that can save
37 humanity from burnout in the longer term, minimizing damage from CO₂ emissions by keeping
38 them out of the atmosphere. Metal-organic frameworks (MOFs) have received a promising career
39 for CO₂ capture due to their high porosity, surface area, excellent metal-to-legends interaction,
40 and good affinity to capture CO₂ molecules. On the other hand, Ionic liquids (ILs) as emerging
41 solvents have reported a significant influence on CO₂ solubility due to their wide range of
42 tunability in the selection of a variety of cations and anions along with the advantage of non-
43 volatility, high thermal stability, nonflammability. The current review highlights the recent
44 progress and ongoing careers of employing MOFs and ILs in carbon capture technologies before
45 their commercialization on a large scale. A brief overview of CO₂ capturing using MOFs and ILs
46 is given under the influence of their possible functionalization to enhance their CO₂ separation.
47 Information on the possible integration of MOFs-ILs as a composite system or membrane-based
48 gas separation is also presented in detail. The integration has a high potential to capture CO₂ while
49 minimizing the unit operation costs for a stable, efficient, and smooth industrial gas separation
50 operation. Present work attempts to link the chemistry of MOF and IL and their successful
51 hybridization (MOF-IL composite) to process the economics for CO₂ capture.

52 **Keywords:** *MOFs, ILs, CO₂ capture, MOFs-IL composite systems, membranes*

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63 **1. Introduction**

64 The high consumption of fossil fuels with the rapid growth in industrialization and urbanization
65 produces a significant amount of carbon dioxide (CO₂) in the surroundings.² The “CO₂ emissions”
66 word has become a buzzword in recent years due to its anthropogenic role in increasing the global
67 earth’s temperature. Moreover, CO₂ has made the natural disaster worse.³ According to the recent
68 global monitoring report, the average CO₂ atmospheric concentration of 417.06 parts per million
69 (ppm) was recorded in the year 2022, with a high global growth rate of 2.13 ppm reported
70 between the years 2021-2022.⁴ The excessive release of CO₂ produces several environmental
71 problems such as rising sea levels, global warming, ecosystem disorder, relocation of wildlife
72 inhabitants, and adverse effects on human lives.⁵ This has raised the alarm for all the countries to
73 devise a methodology for CO₂ capture. Most of the efforts on CO₂ capturing are focused on
74 sequestering CO₂ from large-point sources like power plants and the process industries. The
75 technologies used to produce heat and electricity from fossil fuels determine the requirements for
76 CO₂ capture.^{6,7}

77 To capture CO₂, numerous technologies are widely used in this field, including post-combustion,
78 pre-combustion, and oxyfuel combustion, as shown in Fig. **S1**. The post-combustion conditions
79 require complete fuel burning in a single step. This results in the release of excessive heat to
80 generate steam at high pressure, which can then be used to drive a steam turbine for electricity
81 generation.⁸ The flue gas exposed to about 10-16% CO₂ after processing is released into the
82 environment without involving a proper carbon-capturing system.⁹ The pre-combustion
83 mechanism involves gasifying fuel (coal, oil, etc.), including pure oxygen, and steam to form
84 syngas.¹⁰ During the water-gas shift (WGS) reaction process, the syngas, which are made up of
85 hydrogen (H₂) and carbon monoxide (CO), go through purification before it goes into the
86 reactor.¹¹ The WGS reactor converts CO into H₂ and CO₂ by reacting with steam, producing both
87 the steam and CO, which go under desulfurization before going to the WGS reactor as per their
88 requirements.¹² This stage of the process involves the gas mainly composed of H₂ and CO₂ which
89 results in the capture of CO₂ and combustion of H₂ in a gas turbine utilized to generate heat and
90 electricity.¹³ The oxyfuel-combustion involves pure oxygen for combustion instead of using air.
91 The heat released from this process is required to generate steam at high-pressure to run a steam
92 turbine for electricity generation. For easier separation of CO₂ and water vapors, this type of

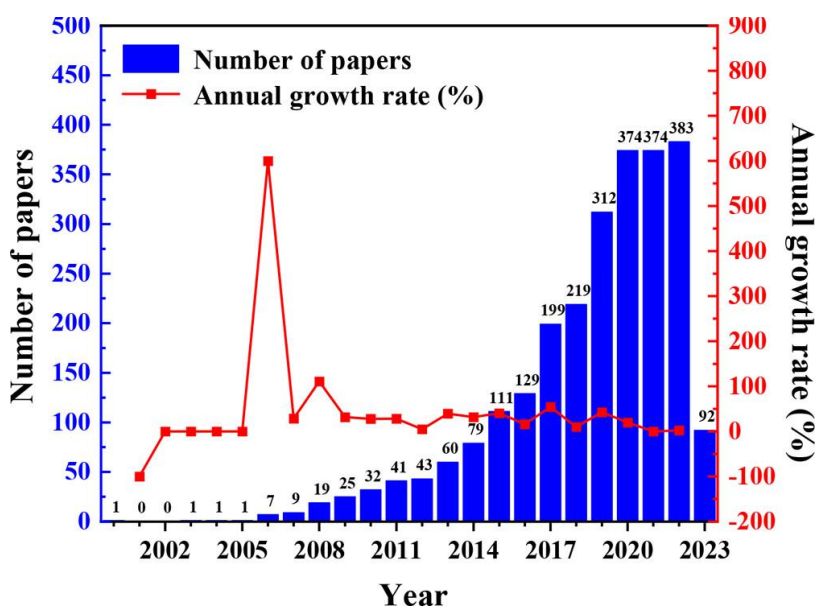
93 nitrogen (N₂) free combustion system uses a flue gas predominantly composed of concentrated
 94 CO₂ and water vapors. Oxy-combustion does not require the capture of CO₂ from the process of
 95 combustion process because the hydrocarbon fumes can easily be purified by their condensation.¹⁴
 96 **Table 1.** summarizes the typical conditions for each process.

97 **Table 1.** Typical conditions for pre-combustion, post-combustion, and natural gas sweetening. Reproduced with
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	Pre-Combustion ^a	Post-Combustion	Natural Gas Sweetening
Gas Composition (mole)			
N ₂	3.90%	70-75%	0-0.2%
H ₂	55.50%		
H ₂ O	0.14%	5-10%	
CO	1.70%	20 ppm	
O ₂		3-4%	
CO ₂	10-15%	37.70%	0.1-8%
SO _x		<500 ppm	
NO _x		<800 ppm	
H ₂ S	0.40%		0-15%
C ₂ +			0-15%
CH ₄			70-95%
Condition			
Pressure (bar)	30	1	5-120
Temperature (°C)	40	40-75	30-40
^a After the water-gas shift reaction			

99 Post-combustion CO₂ capture is a broadly used technique that can easily be adapted to existing
 100 power plants, rather than relying on pre-combustion or oxyfuel combustion systems. **Fig. S2**
 101 describes some of the current post-combustion means used to capture CO₂. Cryogenics,
 102 absorption, adsorption with physiochemical means, and membrane-based methods are all part of
 103 this category.¹⁵ Post-combustion techniques utilizing amines-based solvents have become a
 104 widely accepted remedy to overcome CO₂ emissions because amines are highly thermally stable
 105 and reactive, which makes them able to assist CO₂ absorption effectively.¹⁶ The adsorption based
 106 on amines is done with a tall absorption column, which requires high capital expenditures.¹⁷
 107 Moreover, amines are degraded in flue gases because of oxygen (O₂), sulfur dioxide (SiO₂), and
 108 nitrogen dioxide (NO₂) impurities, which can result in corroding the absorption column.¹⁸ Based
 109 on the discussion above, it can be said that amines-based absorption is an efficient method to
 110 capture CO₂ from the environment. It can seem that the major downside of the amine process is

111 that the organic solvent is amine-based which can create a problem with the process of
112 regeneration due to the chemical reaction in the amine.



113
114 **Fig 1.** No's of publications featuring the keywords “metal-organic framework and ionic liquid” as a function of the
115 year. Source: Web of Science. With permission from Ref.¹⁹ Copyright 2023, American Chemical Society

116 An immense amount of highly critical and technical literature is available in support of CO₂
117 capture through different ways including MOFs and ILs. **Fig 1.** shows the data of the number of
118 publications reported featuring the keywords “metal-organic framework and ionic liquid” by Web
119 of Science. Liu et al.²⁰ presented a state-of-the-art review on improvement in rational design and
120 functionalization of MOFs to enhance the CO₂ capture and conversion through MOFs based
121 composites. Younas et al.²¹ and Ding et al.²² reviewed MOF's thermal, chemical, and mechanical
122 stability improvements via novo synthesis and post-synthesis structural processing. Christopher et
123 al.²³ presented the structural and chemical properties of MOFs which could lead to the high
124 capture and catalytic conversion of CO₂. In one of our recent reviews, the enhancement in CO₂
125 capture through employing ILs and DES, their possible functionalization along with their role in
126 the conversion of CO₂ into different valuable products is presented following the highly economic
127 prospect of employing both solvents for CO₂ capture.²⁴ Lian et al.²⁵ reviewed the cost-
128 effectiveness of utilizing ILs based solvents for CO₂ capture through membranes, catalysts, and
129 their hybridization with advanced nanomaterials (MOFs, COFs, graphene, Zeolites, etc.). Other
130 recent notable studies by Guo et al.²⁶, Ullah et al.²⁷, Olabi et al.²⁸, and Ferreira et al.²⁹ that cover

131 the synthesis of MOFs, ILs, and their hybridized composite systems (MOF-IL) mechanism for
 132 CO₂ capture, along with their effective utilization in membranes-based gas separation
 133 technologies are worthwhile references to develop a basic understanding of the individual topics.

134 The current review highlights the significance, advancement, and ongoing careers of employing
 135 MOFs, ILs, and their hybrid systems (MOF-IL composites) in carbon-capturing technologies. A
 136 comprehensive overview of CO₂ capture technologies is provided starting from the post-
 137 combustion, pre-combustion, and oxy-fuel combustion. The successful utilization of MOFs and
 138 ILs through composite membrane systems greatly enhances CO₂-capturing performance. In
 139 addition, the successful functionalization of MOFs with (amino/fluorine/adenine groups and
 140 pillared layer, etc.) and ILs with (amine, carbonate, ether, and carboxyl groups) has a great
 141 affinity towards improving the CO₂ separation. The synthesis of low-cost, sustainable, and
 142 environment-friendly mass production MOF-IL integration could be significant for their large-
 143 scale production and commercialization. The successful integration of MOFs-ILs has a high
 144 potential for CO₂ capturing systems with the advantage to minimize the unit operations operating
 145 costs for a stable, efficient, and smooth operation for industrial gas separation. An evaluation of
 146 MOFs and ILs properties compared to other absorbents is summarized in **Table 2**.

147 **Table 2.** Advantages and Disadvantages of utilizing MOFs³⁰ and ILs³¹ with Biphasic solvents³², MEA³³, and DESs³⁴

Biphasic solvents	MEA	DESs	MOFs	ILs
Advantages				
Low viscosity and low energy consumption	Low price, High thermal stable, and reactive solvents	Low corrosion, Nonvolatility, Nontoxic, High solubility, Inexpensive, Inflammable, and biodegradable nature, Eco-friendly	Low heat capacity, Regeneration requires Low energy consumption	low corrosion, high solubility, and Nonvolatile
Disadvantages				
Complex equipment	High volatility, corrosion, and high energy consumption	High viscosity, the synthesis cost for some deep eutectic solvents is highly expensive.	Requires high cost for synthesis and regeneration, unavailability, and costliness of raw materials	Biototoxicity, high price, and high viscosity
MEA: Monoethanol amine; DES: Deep eutectic solvents; MOFs: Metal-organic frameworks; ILs: Ionic Liquids				

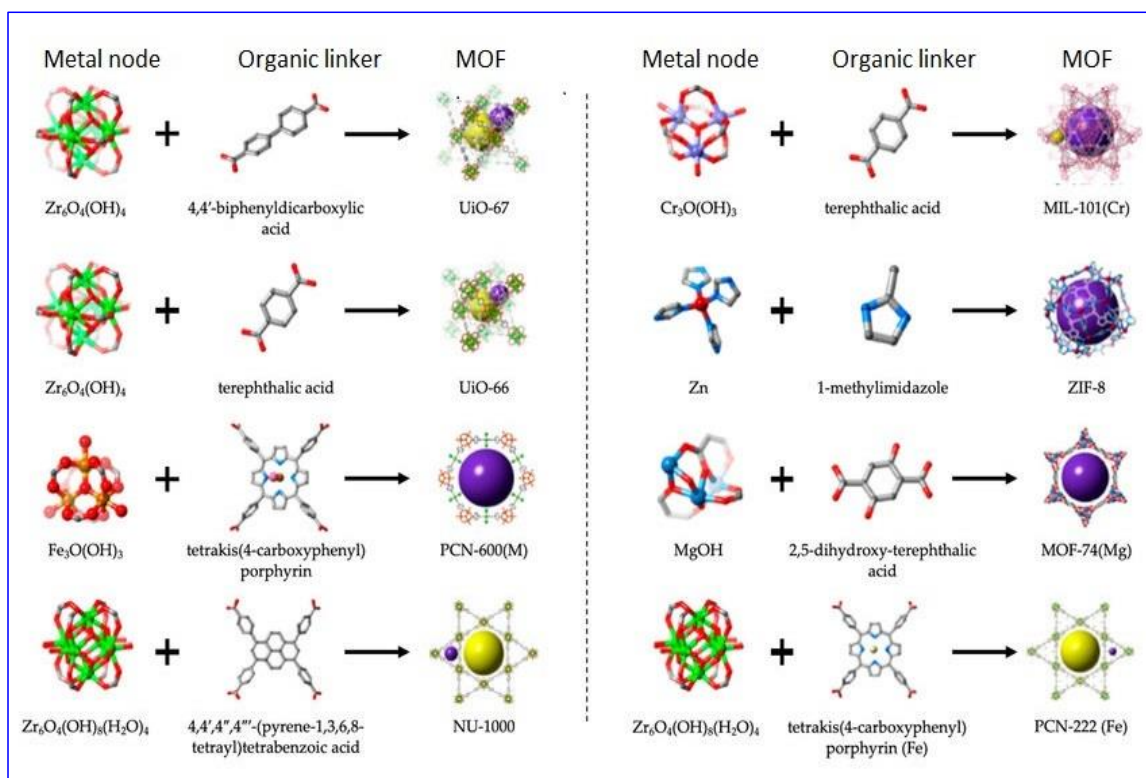
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149 **2. MOFs**

150 MOFs are the advanced class of coordinate polymers/networks whose framework is composed of
 151 metal ion clusters carrying nodal framework positions associated with bi, tri, and multi-podal

152 organic ligands. The transition metal elements that can be utilized are di-valent (Mg, Zn, Cu, etc),
153 tri-valent (Al, Fe, Cr, etc), and tetravalent (V, Ti, Hf, Zr, etc). In contrast, legends moieties can be
154 taken from imidazolate, pyrazolate, carboxylate, and phosphonate families that can be attached
155 with different lengths and functional groups to give better and more selective absorption towards
156 the targeted gas molecule. **Fig 2.**³⁵ shows examples of various MOFs and their corresponding
157 metal nodes and linkers.

158 MOFs are porous crystalline nano-structures with the advanced feature of high surface area and
159 strong metal-to-legend interaction ³⁶. MOFs show an outstanding degree of tunability with the
160 wide variety of organic and inorganic components that can be involved via post-synthetic
161 modification of their structures.³⁷ The MOF's high tunability makes it possible to design and
162 control its structural aspects such as pore size, geometry, surface area, and surface chemistry more
163 preciously than other materials.³⁸ Due to these properties, it displays unsurpassed adsorptive and
164 catalytic abilities, including carbon-capturing, energy storage, decomposing volatile chemicals,
165 and environmental applications.³⁹ There is a wide range of literature available on the use of MOFs
166 as selective adsorbents of different gases using molecular.⁴⁰ Therefore, it implies that to pass
167 through the pores of MOF, molecules must have an appropriate pore kinetic diameter as listed in
168 **Table 3.**



169

170 **Fig 2.** Examples of different MOFs with their corresponding metal nodes and linkers. Reproduced with permission
 171 from Ref.⁴¹ Copyright 2017, American Chemical Society

172 **Table 3.** Kinetic diameter of different gas molecules. With permission from Ref.⁴² Copyright 2001, Elsevier

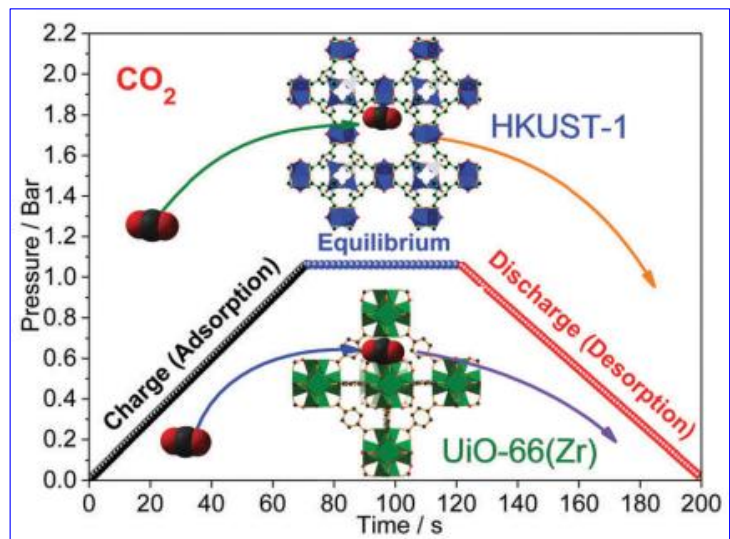
Molecule	Kinetic Diameter (Å)
N ₂	3.64
H ₂	2.89
H ₂ O	2.65
CH ₄	3.8
O ₂	3.46
CO ₂	3.3

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174 2.1. CO₂ Adsorption Mechanism in MOFs

175 The capacity of CO₂ adsorption in porous materials mainly depends upon the surface area of
 176 adsorbents.⁴³ Numerous adsorbents with higher surface areas like zeolites, carbons, and MXanes
 177 were reported in the literature to adsorb gases at various concentrations from different sources.⁴⁴
 178 MOFs have gotten great attention for CO₂ uptake due to their good chemistry, structural
 179 tunability, and better adsorbate-adsorbent interactions with CO₂ through the open metal site.⁴⁵
 180 Additionally, the properties of MOFs like inner surface polarity, the topology of the framework,
 181 pore size, and surface area could be tuned for the adsorption of CO₂ through the careful selection

182 of metal centers and organic linkers.⁴⁶ The process of CO₂ adsorption-desorption in MOFs is
183 shown in **Fig 3**.



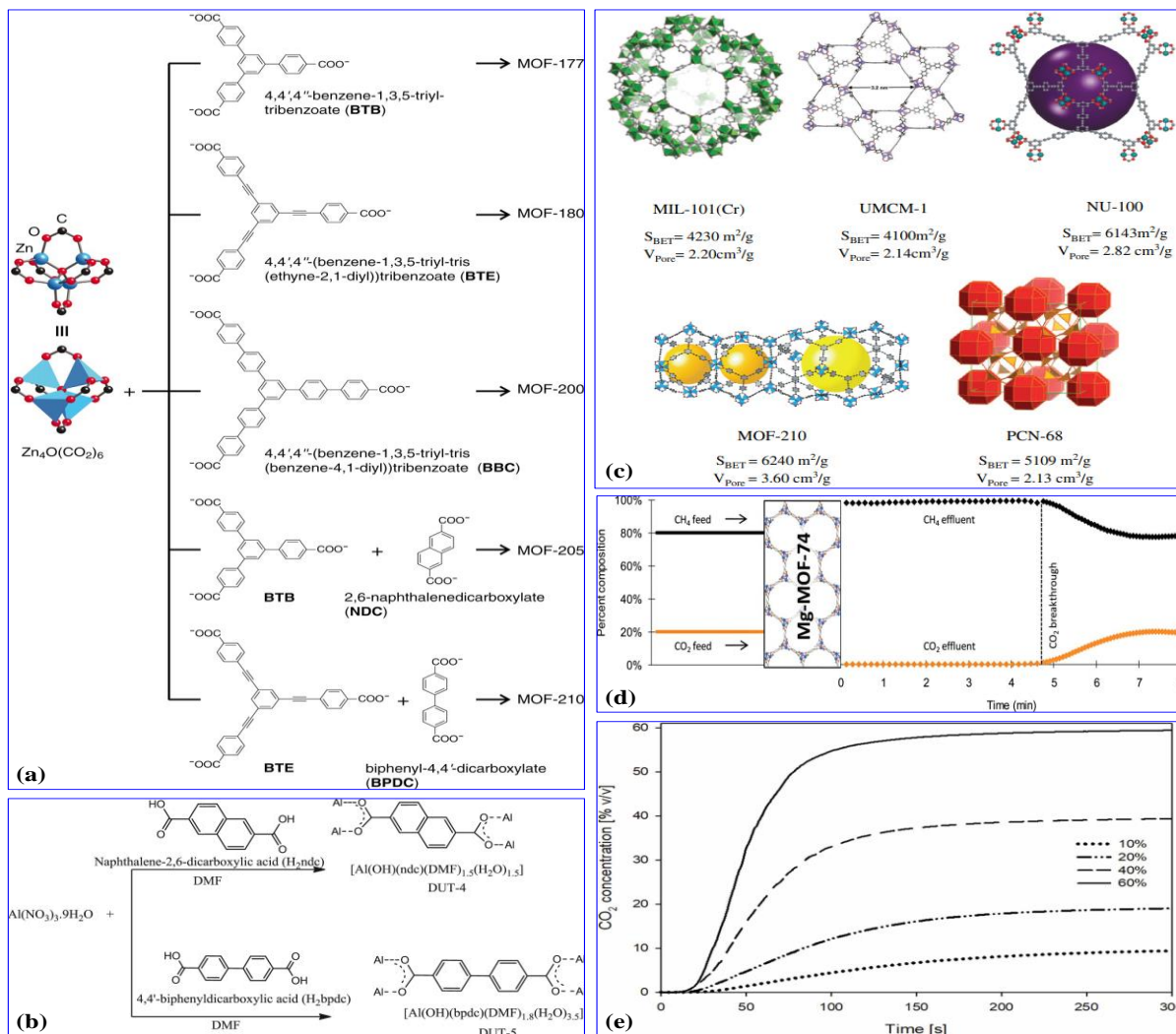
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185 **Fig 3.** Illustration of CO₂ adsorption-desorption in MOFs. With permission from Ref.⁴⁷ Copyright 2017, Royal
186 Society of Chemistry

187 The hierarchical nanostructures have recently received great attention to enhance the dynamic
188 capacity and selectivity of MOFs by creating larger pore sizes or hollow structures. The
189 hierarchical porosity from the micro- to mesoscale uses intrinsic pores of MOFs to provide higher
190 exposure to the gas molecule, which can also effectively accelerate the mass diffusion/permeation
191 and avoid blocking the micropores. Larger-sized meso and macro-porous channels also provide
192 enough space to load functional groups to further enhance the separation efficiency.⁴⁸ Qiu et al.⁴⁹
193 used, a one-pot synthesis strategy to fabricate a hierarchically porous Cu-BTC MOFs for the
194 selective separation of CO₂ which showed abundant mesopores and outstanding dynamic CO₂/N₂
195 separation (56.547) along with the good CO₂ uptake of (8.054 mmol.g⁻¹) and (4.200 mmol.g⁻¹) at
196 273K and 295K respectively with the feed pressure of 1 bar. Yurdusen et al.⁵⁰ investigated the
197 role of introducing narrow micropores on the CO₂ adsorption capacity of MOF-MIL-88B by the
198 control of hierarchical pores via Fe-BDC ratio into MOF. They reported that the ultra-micropore,
199 macropore, and mesopore volumes were successfully improved through the formation of
200 hierarchical pores and controlling the textural mesoporosity via the Fe/BDC ratio into MOF-MIL-
201 88B which improved the CO₂ adsorption capacity of MIL-88B by a factor of 2.1 with the CO₂
202 uptake of (1.27 mmol.g⁻¹), (2.27 mmol.g⁻¹), and (2.77 mmol.g⁻¹) at 298K with the feed pressure of
203 1bar, 3bar, and 5bar respectively higher than CO₂ adsorption of commercially available MOFs.⁵¹

204 ⁵² The most important property of MOF material is pore size which ultimately effects the catalytic
205 conversion of CO₂, its separation, and adsorption.⁵³ MOFs form a porous structure after the
206 evacuation of solvent molecules. To increase the selective adsorption of CO₂ from the mixed gas
207 composition of CO₂/CH₄ and CO₂/N₂ under humid conditions, it is possible to make a compound
208 that can trap guest molecules in its channel during sample preparation which gives the creation of
209 narrow pores (np), and then ultimately reduces the pore size of the MOFs.⁵⁴ Furukawa et al.⁵⁵
210 formed MOFs with extremely high porosity, comprised of Zn₄O(CO₂)₆ units with modification of
211 organic ligands as shown in **Fig 4a**. Among all the series, MOF-210 displayed the largest
212 “Langmuir and BET surface areas” of about (10,400 m².g⁻¹ and 6240 m².g⁻¹) with pore volumes of
213 (0.89 cm³.g⁻¹ and 3.60 cm³ .g⁻¹) of MOF crystal.⁵⁵ Senkovska et al.⁵⁶ reacted Al(NO₃)₃.9H₂O with
214 legends 4,4'-biphenyl dicarboxylate (bpdc) and 2,6-naphthalene dicarboxylate (ndc) with N, N-
215 dimethylformamide (DMF) under the hydro-solvothermal reaction to produce porous frameworks
216 with the formulas [Al (OH)(bpdc)(DMF)_{1.8}(H₂O)_{3.5}] (DUT-5) and [Al(OH)(ndc)(DMF)_{1.5}(H₂O)_{1.5}]
217 (DUT-4) with the structures shown in **Fig 4b**. According to reports, DUT-4 and DUT-5 attained
218 the BET pore volumes and surface areas of about 0.68 cm³.g⁻¹,1308 m².g⁻¹, and 0.81 cm³.g⁻¹,1613
219 m².g⁻¹ respectively. DUT-4 has achieved the CO₂ uptake capacity of 8.17 mmol.g⁻¹ at 10 bars,
220 which is more analogous with the CO₂ uptake capacity of MIL-53 (Al).⁵⁶

221 The specific surface area is another significant factor that helps in assessing the catalytic
222 performance and adsorption capacity of MOF.⁵⁷ **Fig 4c**. shows the crystal structure of various
223 MOFs with different pore volumes and surface areas reported by Chen et al.⁵⁸ The high pore size
224 and surface area of MOF structure favors the high adsorption to facilitate the high capture of CO₂
225 through the porous cage of MOF. The first comprehensive study to find the relation between CO₂
226 capacity and the surface area was performed by Yaghi’s group.⁵⁹ This collection includes MOFs
227 with a variety of properties, comprising pores with open metal sites (Cu₃(BTC)₂ and MOF-505),
228 square channels (MOF-2), alkyl-functionalized pores (IR-MOF-6 and IR-MOF-3), interpenetrated
229 (IRMOF-11), cylindrical channels packed hexagonally (MOF-74), and the frameworks of higher
230 porosity (MOF-177) and (IRMOF-1). They reported that the MOF-177 exhibited the largest
231 surface area among all materials with a CO₂ uptake of (33.5 mmol.g⁻¹) with 60 wt.% loading at a
232 feed pressure of 35 bar.⁵⁹ **Table 4-5**. shows the capacity of various MOFs for CO₂ uptake at
233 different high and low-pressure conditions respectively.

234 The breakthrough experiment is also considered one of the most precise strategies to determine
235 the separation capacity of CO₂, in which adsorbent with the bed packed is subjected to a two
236 components-divided mixture composition gas stream, and CO₂ release from the substance is
237 monitored.⁶⁰ The breakthrough experiment for Mg-MOF-74 was conducted by Britt et al.⁶¹ with
238 the exposure of MOF to a mixture of 20% CO₂ in CH₄ shown in **Fig 4d**. With an 8.9% dynamic
239 capacity for CO₂ adsorption, the outcomes revealed that the CO₂ adsorption in Mg-MOF-74 is
240 greatly favored over CH₄. The CO₂ breakthrough experiments were conducted on isostructural Zn-
241 MOF-74 to explore the significance of metal ions in CO₂ adsorption. Zn-MOF-74 only absorbs
242 0.35wt.% of CO₂, which is 96% less than Mg-MOF-74, and highlights the advantage of selecting
243 the right metal ions in CO₂ binding. The higher capacity of CO₂ in Mg-MOF-74 is reflected as a
244 good interaction between Mg²⁺ and CO₂.⁶¹ **Fig 4e**. displays different curves for CO₂ breakthrough
245 Xintao samples under the influence of varying the concentration of CO₂ in the feed gas mixture.
246 They found a sigmoidal shape connected with dynamic adsorption processes in fixed beds.
247 Moreover, the rise in the inlet concentration of CO₂ reduces the breakpoint time along with a
248 significant rise in the slope of the curves.⁶²



249

250 **Fig 4. (a)** Zn₄O(CO₂)₆ attached with organic legends to produce MOFs. With permission from Ref.⁵⁵ Copyright 2010,
 251 Science Report **(b)** Synthesis of DUT-4 and DUT-5 through metal Al(NO₃)₃·9H₂O and legend ndc and bpdc. With
 252 permission from Ref.³⁶ Copyright 2018, Elsevier **(c)** Crystal structures of various MOFs with mentioning their pore
 253 volumes and surface areas. With permission from Ref.⁵⁸ Copyright 2016, American Science Publishers **(d)** Schematic
 254 of the breakthrough experiment for Mg-MOF-74 under the exposure of a mixture of 20% CO₂ with CH₄. With
 255 permission from Ref.⁶¹ Copyright 2009, The proceeding of National Academy of Science **(e)** CO₂ breakthrough
 256 curves found for Xintao sample by changing the concentration of CO₂ in the feed gas mixture of CH₄/CO₂ under (T =
 257 303 K, P = 1 atm). With permission from Ref.⁶² Copyright 2021, Elsevier.

258 **Table 4.** CO₂ uptake capacity of various MOFs at high-pressure conditions.

MOF Type	Pressure (bar)	Temperature (K)	CO ₂ Adsorption capacity (mmol.g ⁻¹)	Ref
Cu-BTC	40	303	14.00	63
	10	303	8.07	64
	15	297	11.70	65
MOF-177	14	298	9.02	66

Mg-MOF-74	35	313	15.00	67
	30	303	14.80	68
ZIF-8	40	303	8.60	69
	45	305	9.10	70
UiO-66	60	303	7.65	71
	30	298	7.29	72
IRMOF-11	30	298	14.7	59
HKUST-1	35	298	10.7	73
IR-MOF-1	35	298	21.7	73
MOF-177	35	298	33.5	73
MIL-100(Cr)	50	303	18	73
MIL-101(Cr)	50	303	28	73
MOF-200	50	298	64.3	55
MOF-205	50	298	38.1	55
MOF-210	50	298	65.2	55
Cu ₃ (BTC) ₂	32	298	10.7	55
MOF-177	32	298	33.5	55

259

260 **Table 5.** CO₂ uptake capacity of various MOFs at low pressure.

MOF Type	Pressure (bar)	Temperature (K)	CO ₂ Adsorption capacity (mmol.g ⁻¹)	Ref
HKUST-1	1	295	5.1	74
Cu-BTC	1	298	5.33	75
UMCM-150	1	298	2.6	74
Zeolite 13-X	1	293	1.77	76
MIL-47	1	298	2	74
UTSA-16	1.1	293	3.5	77
MOF-177	1	298	1.6	74
HKUST-1	1	293	3.55	78
Cu-BTC	1	283	7.00	79
Mg-MOF-74	1	298	8.61	80
	1	293	9.02	51
Cu-BTC	1	298	4.26	81
	1	298	5.33	75
	1.2	295	2.46	82
	1	298	3.06	83
Zeolite-13X	1	298	8.07	84
UTSA-16	1.1	298	3.5	77
	1	298	1.59	85
HKUST-1	1	196	7.92	85
	1	298	3.55	85

261

262 Different gas molecules have different strengths of interaction with the adsorbent, hence the
263 mechanism for the selective absorption of CO₂ depends on the interaction between CO₂ and the
264 adsorbent in comparison with the other probe molecules.⁸⁶ The more molecules of CO₂ would be
265 absorbed when the interaction of CO₂ molecules will become stronger in comparison with the
266 other molecules like O₂, N₂, and CH₄.⁸⁷ Mostly the equilibrium-based mechanism depends upon
267 strength regardless of the molecule's uniformity.^{88, 89} The mechanism comprises the capacity of

268 the physical adsorbent to capture CO₂ molecules and drives the selective adsorption of CO₂
269 molecules from the other gases. Fcu-MOFs, rht-MOF-7, and Mg-MOF-74 are a few examples of
270 MOFs that undergo an equilibrium-based adsorption mechanism for the selective separation of
271 CO₂.^{88, 90} Contrary to this, the mechanism of kinetic sieving is used where the molecular size of
272 gas becomes closer or quite similar to the size of the CO₂ molecule.^{62, 91}

273 Another famous technique for separating CO₂ is “kinetics-driven sieving” used where the
274 molecular size of CO₂ resembles the size of O₂, CH₄, and N₂.⁹² However, finding a MOF that
275 selectively absorbs CO₂ from the exhaust stream is quite challenging. So, the proper selection of
276 MOFs counts a lot for the efficient and selective separation of a targeted gas molecule. However,
277 combining two adsorption sites has proven to be quite an efficient approach in favor of getting
278 MOFs for high CO₂ capturing. An experimental study conducted by Li et al.⁹³ showed an easy
279 condensation reflux method to examine the mechanism of CO₂ adsorption on the surface of MOF-
280 74 (Ni). After varying the temperature and synthesis time, they discovered that the structure of
281 MOF-74(Ni) and the isosteric heat for the adsorption of CO₂ can be tuned consequently. The
282 modified MOF-74(Ni)-24-140 prepared under the temperature of 140 °C for 24 h exhibited an
283 optimized CO₂ adsorption capacity of about 8.29/6.61 mmol.g⁻¹ at the temperature of 273/298 K
284 under 1 bar feed pressure, which was (1.5/1.6 times) higher than previously reported UTSA-16,
285 (2.0/2.1 times) than MOF-74-Ni and (3.6/4.9 times) DA-CMP-1 under similar conditions.⁹³

286 The quantitative structures–property relationship (QSPR) is the strategy recently reported to
287 develop a strong relationship between MOF-CO₂ for the prediction of their CO₂ capture
288 performance. In one of the recent studies Ahmadi et al.⁹⁴ based on applying the quasi-SMILES
289 parameters such as specific surface area, temperature, BET, pore volume, and pressure to predict
290 the CO₂ uptake of MOFs. The data set includes 260 quasi-SMILES individualities of MOFs that
291 were experienced in training, validation, and testing three times. As a result of the QSPR model
292 interpretation, the outcomes of the impact of temperature and pressure for CO₂ adsorption using
293 the relationship approach are quite closer to the experimental observation of CO₂ capture.
294 Furthermore, the model gives the strong response of adding functional groups containing N, O,
295 and double bonds to the organic linkers of MOFs to improve the MOF-CO₂ interaction along with
296 the high uptake in CO₂ adsorption characteristics.⁹⁴

297

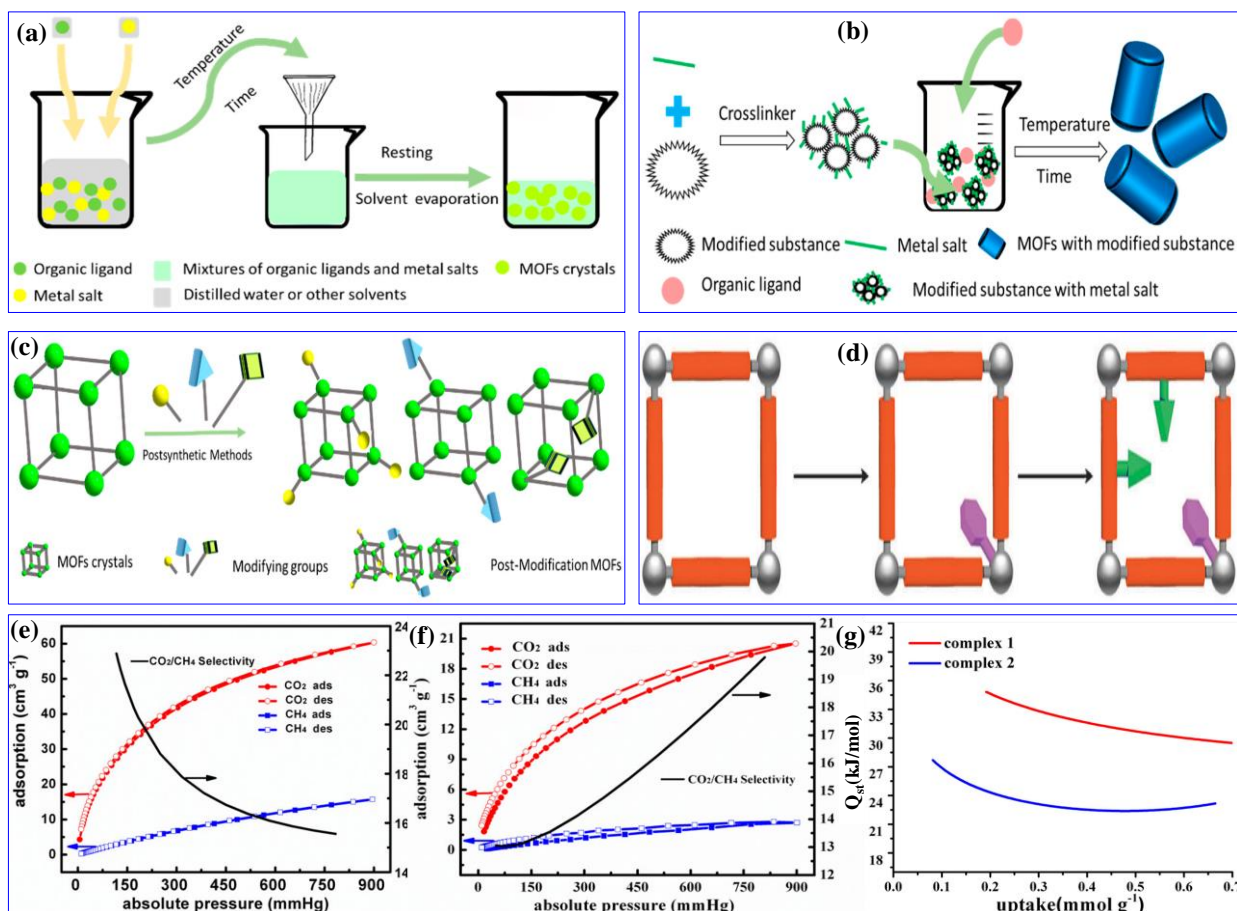
298 2.2. Functionalization of MOFs to CO₂ capture

299 Typically, organic molecules that possess N-donor or O-donor atoms are commonly employed as
300 ligands to connect the metal ions in MOFs. These ligands encompass carboxylates (aliphatic or
301 aromatic), pyridyl groups (such as pyrazine and derivatives of 4,4'-bipyridyl), cyano compounds,
302 polyamines formed from imidazole, oxalic acid, and benzene, as well as phosphonates, sulfonates,
303 and crown ethers.⁹⁵ The perception of functionalizing of MOFs is associated with two approaches
304 including pre-synthesis functionalization (use of linkers containing functional groups before the
305 MOF synthesis) and post-synthesis functionalization (use of functional groups after the MOF
306 synthesis). The schematic for the synthesis of MOFs by conventional and through involving
307 pre/post-synthesis modification is shown in **Fig 5a-c** respectively.⁹⁶

308 The pre-synthesis ligand functionalization has a significant effect on improving the affinity of
309 MOFs towards CO₂ adsorption and separation.⁹⁷ This method is advantageous for achieving high
310 CO₂ storage properties due to its easy modification procedure along with the advantage of
311 combining a variety of functional groups.⁹⁸ To develop the IRMOF series, Yaghi's group
312 integrated R-BDC with N, N-diethyl formamide (DEF), and zinc nitrate tetrahydrate under
313 solvothermal conditions.⁹⁹ According to the report, the IRMOFs pore diameter changes from 12.8
314 nm to 28.8 nm with the introduction of functional groups (R-) such as -C₂H₄, -OC₃H₇, -NH₂, and
315 -Br.¹⁰⁰ Similarly, Cu-PCN-68 is another Cu-based MOF with the formula of [(Cu₃(H₂O)₃-
316 (ptei).13H₂O.33dmf)] was identified with the capacity of 30.4 mmol.g⁻¹ to uptake CO₂ at 35 bar
317 and 298 K with a pore volume and BET surface area of "2.13 cm³.g⁻¹" and "5109 m².g⁻¹"
318 respectively.¹⁰¹

319 In contrast to other methods of modification "amine-functionalized legends" are more attractive
320 because of their higher affinity for CO₂ selectivity and adsorption.¹⁰² According to this approach,
321 CO₂ molecules behave as "Lewis acid" and amine molecules as "Lewis base".¹⁰³ The amine-
322 functionalized MIL101 (Cr) formed by Lin et al.¹⁰⁴ had an average particle size of 50 nm with an
323 area of 1675 m².g⁻¹. The synthesized MOFs exhibited a CO₂-capturing capacity of 15 mmol.g⁻¹ at
324 a pressure of 25 bar at 289 K.¹⁰⁴ In another study conducted by Ko et al.¹⁰⁵, SBA-15 silica was
325 synthesized and grafted with amines (tertiary, secondary, and primary,) which exhibited CO₂
326 capacities of about 0.17, 0.75, and 0.95 mmol/g, respectively.¹⁰⁵ The mechanism of functional
327 group grafting through bi-functional MOF with the legend is shown in **Fig 5d**. Using an amine-

328 functionalized Ti-based MOF, Wan et al.¹⁰⁶ synthesized stable and highly stable molecules (MIP-
329 207-NH₂-n). They found that the addition of amino groups (n=25wt.%) in MOF (MIP-207-NH₂-
330 25%) successfully enhanced the CO₂ separation to (3.96 and 2.91 mmol.g⁻¹) which is (20.7% and
331 43.3%) better as compared with the un-modified MOF at the temperature of about 0°C and 25°C
332 respectively. In addition to this, the breakthrough experiments also resulted in the separation
333 factor (CO₂/N₂) and adsorption capacity for CO₂ increased by 15% and 25% respectively.¹⁰⁶
334 Through the use of linker 2-amino terephthalic acid, Abid et al.¹⁰⁷ prepared Zr-MOF nanoparticles
335 functionalized with amino acid and found that the Amino-Zr-MOF showed BET and Langmuir
336 surface area of about 1220 m².g⁻¹ and 1395 m².g⁻¹ when activated at 200 degrees Celsius.
337 According to the results, the total pore volume, and the average pore radius were "0.611cm³.g⁻¹"
338 "nd "0.9" nm" respectively. It was observed that amino-Zr-MOF showed higher CO₂ adsorption
339 (4.46 mmol.g⁻¹) as compared with the CO₂ adsorption achieved through Zr-MOF (3.52 mmol.g⁻¹)
340 at feed pressure of 1bar and temperature 273K. Moreover, a higher CO₂/CH₄ selectivity and
341 greater thermal stability were reported for the amino-Zr-MOF with high heat of CO₂ adsorption
342 (29.4 kJ.mol⁻¹).¹⁰⁷



343

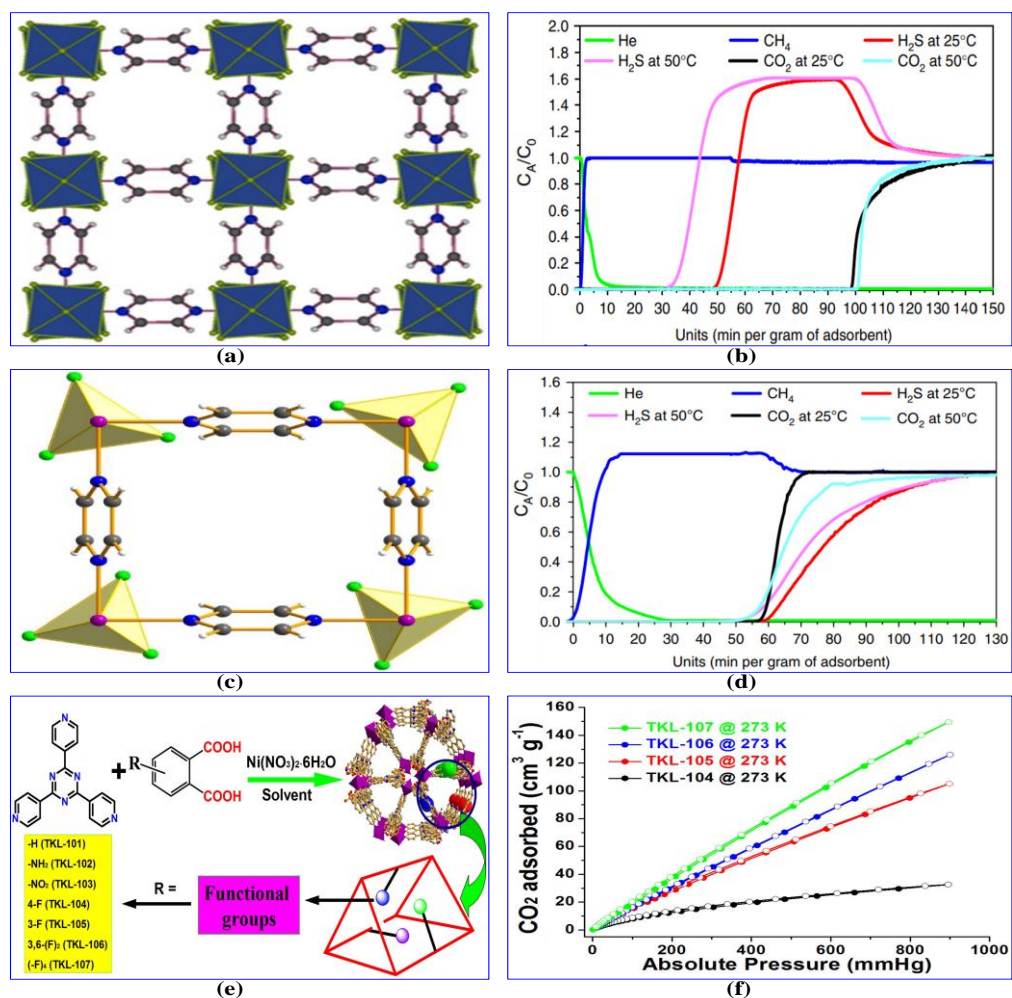
344 **Fig 5.** Schematic representation for the synthesis of MOF through (a) Conventional method (b) Pre-synthesis
 345 modification (c) post-synthesis modification. Reprinted from Ref.¹⁰⁸ Permission not required. (d) The mechanism
 346 of functional group grafting through bi-functional MOF with the legend, the orange pillar donates the organic
 347 ligand, the grey ball represents metal and lavender, and the green bar donates the functional groups With
 348 permission from Ref.¹⁰⁹ Copyright 2012, Royal Society of Chemistry (e) CO₂ and CH₄ desorption/adsorption
 349 capacities and selectivity from their equimolar mixture for complex-1 at 273K (f) CO₂ and CH₄
 350 desorption/adsorption capacities and selectivity from their equimolar mixture complex-2 at 298K (g) CO₂
 351 adsorption enthalpies for both complexes 1 and 2. With permission from Ref.¹¹⁰ Copyright 2014, American
 352 Chemical Society

353 The synthesis of MOFs by pillared layer functionalization is an effective pre-synthesis strategy to
 354 enhance CO₂ capture.¹¹¹ The pillared layer in MOF gives an enhanced surface area to MOF, and
 355 the presence of an amino-functional group in the pillar can also increase CO₂ affinity. In recent
 356 years, there have been promising results achieved regarding utilizing pillared-layer MOFs for the
 357 storage and adsorption of different gases like O₂, CH₄, and CO₂ from the aqueous solutions.¹¹²
 358 According to Amer's research, an attempt was made to examine the effectiveness of two MOFs
 359 with different pillared layers namely (Co)₂(BDC)₂(DABCO) and Zn₂(BDC)₂(DABCO) for CO₂

360 separation. Both the MOFs Co-BDC-DABCO and Zn-BDC-DABCO exhibited a high capacity for
361 CO₂ uptake to about (4.4 mmol.g⁻¹ and 6.3 mmol.g⁻¹) respectively which confirmed a significant
362 improvement in CO₂ uptake when compared with (0.67 mmol.g⁻¹ and 0.95 mmol.g⁻¹) CO₂ for
363 Co-BDC and Zn-BDC respectively.¹¹³ Similarly in another study, DABCO-based MOFs such as
364 (Ni-DABCO and Cu-DABCO) exhibited CO₂ uptake capacities of (2.2 mmol.g⁻¹ and 1.4
365 mmol.g⁻¹) respectively.¹¹⁴ In one of the studies conducted by Xuan et al.¹¹⁰ two “pillar-layered”
366 MOFs were synthesized namely {[Zn₂(bpta)(bpy-ea)-(H₂O)].2DMF·H₂O}_n and {[Zn₄(bpta)₂(4-
367 pna)₂(H₂O)₂].4DMF.3H₂O}_n. using the pillar legends N-(4-pyridyl) isonicotinamide (4-pna) and
368 1,2-bis(4-pyridyl)ethane (bpy-ea). The isotherms of CO₂ adsorption/desorption and selectivity for
369 these complexes (1 and 2) were measured at the temperature of 273 K and 298 K as shown in **Fig**
370 **5e** and **Fig 5f** respectively. The enthalpies of CO₂ adsorption (Q_{st}) for both complexes are shown
371 in **Fig 5g**. The complex-1 showed the maximum adsorption for CO₂ nearly 2.69 mmol.g⁻¹ at
372 1.2bar/273 K and 1.87 mmol.g⁻¹ at 298 K. Complex 2 showed CO₂ uptake of 0.91 mmol.g⁻¹ at
373 273 K and 0.66 mmol. g⁻¹ at 298 K. In these experiments, it was shown that MOFs with pillar
374 layers adsorb CO₂ more efficiently.¹¹⁰ In addition, adenine groups are strong candidates for ligand
375 functionalization due to their structural un-coordination.¹¹⁵ Adenine can be utilized to generate the
376 MOFs for several reasons described here: (1) the structure of adenine allows MOF diversity due to
377 the different positions of nitrogen. (2) Adenine has a stiff structure so a strong framework could
378 be attained. (3) The atoms of adenine are co-planar means that the interaction inter-ligand (π-π)
379 could be possible during MOF formation.^{116, 117} These remarkable characteristics make adenine an
380 efficient building block that could be utilized for the construction of various MOFs for the
381 adsorption of CO₂.¹¹⁸ An et al.¹¹⁶ investigated the effect of adenine groups on the bio-MOF-11
382 (CO₂(ad).2(CO₂CH₃)₂.2DMF.0.5H₂O). The experimental results showed that at the feed pressure
383 of 1bar, the CO₂ adsorption capacity of MOF was reported to be high as (4.1 mmol.g⁻¹) at 298 K,
384 with isosteric heat (45 kJ.mol⁻¹) along with the high CO₂/N₂ selectivity of 75 at 298K and 81 at
385 273K. Along with the amino group and Lewis base pyrimidine of adenine in the structure, these
386 favorable properties of CO₂ uptake contributed to the dimension of the pores.¹¹⁶

387 Comparing organic fluorinated compounds to their non-fluorinated counterparts, organic
388 fluorinated compounds demonstrate unusual properties and behaviors due to their C-F bond
389 strength being relatively higher than their C-H counterparts, and their large number of non-

390 bonding p electrons which behave as a shield for carbon backbone. A high electronegativity of
391 fluorine may account for C-F stronger bond.¹¹⁹ The effect of the functionalization of fluorine on
392 the properties of MOF was studied by Galli et al.¹²⁰ They made fluorinated-MOF-1 using the
393 metal precursor, silver (I), and 3,5-bis-(trifluoromethyl)-1,2,4-triazole (Tz). A comparison has
394 been made between the properties of the fluoro-coated MOFs with cavities and the non-fluoro
395 counterparts. The fluoro-coated MOFs exhibit high CO₂ affinity, catalytic activity, thermal
396 stability, and gas selectivity.¹²¹ Belmabkhout et al.¹²² investigated the phenomena of simultaneous
397 removal of CO₂ and H₂S from natural gas. During the experiments, the SIFSIX-3-Ni and
398 NbOFFIVE-1-Ni MOFs were found to be highly CO₂ selective, with a selectivity greater than one
399 for CO₂/H₂S. Additionally, AIOFFIVE-1-Ni showed a good affinity for separating both H₂S and
400 CO₂ from different gas stream compositions under different temperature ranges. **Fig 6a-b.** shows
401 the crystal structure and column breakthrough tests using CO₂/H₂S/CH₄ of NbOFFIVE-1-Ni
402 whereas **Fig 6c-d** shows, the crystal structure of dehydrated AIOFFIVE-1-Ni respectively. As a
403 result of the simultaneous adsorption of H₂S and CO₂, AIOFFIVE-1-Ni exhibited H₂S/CO₂
404 selectivity of (1/1).¹²² Through ligand-functionalization, Zhang et al.¹²³ prepared MOFs, in which
405 different functional groups were introduced to the ligand of ophthalic acid (-NH₂, -NO₂, and F).
406 They resulted that, the introduction of pore wall fluorination in the framework successfully
407 improved the material stability of the MOFs. There was a great enhancement in the results
408 observed with the fluorinated MOFs along with different substituted fluorine atom numbers and
409 positions namely TKL-(104-107), which were found to have good uptake capacity for CO₂ based
410 on their degree of fluoridation.¹²³ **Fig 6e.** shows the general routes for the preparation of TKL-
411 MOFs. The isotherms for CO₂ adsorption were determined to study the ability to capture CO₂ of
412 these fluorine-functionalized MOFs. TKL-107 can capture 150 cm³g⁻¹ (6.69 mmol.g⁻¹) of CO₂ at
413 1.2 bar and 273 K. TKL-105 and TKL-106 showed a large amount of CO₂ adsorption of about
414 (105 cm³g⁻¹ (4.64 mmol.g⁻¹) and 126 cm³g⁻¹ (5.62 mmol.g⁻¹) at 273 K and 1.2 bar, respectively) as
415 shown in **Fig 6f.** The order for CO₂ uptake showed that TKL-107 achieved a higher CO₂ uptake
416 than TKL-106 and TKL-105 which shows that these materials can adjust their CO₂ adsorption
417 system depending on the degree of fluoride modification they possess: the more the fluoride
418 atoms of framework owns the greater capacity for CO₂ uptake.^{123, 124}



419
 420 **Fig 6.** (a) NbOFFIVE-1-Ni crystalline structure in which blue poly-hedra represents NbOF_5^{2-} pillar whereas other
 421 atoms were shown in CPK coloring scheme. (b) Column breakthrough tests through gas mixture with composition
 422 (5/5/90) for $\text{CO}_2/\text{H}_2\text{S}/\text{CH}_4$ with the flowrate of $10 \text{ cm}^3 \text{ min}^{-1}$ on NbOFFIVE-1-Ni at 25°C and 50°C (1 bar), referring
 423 to the influence of different adsorption temperature against response time of various gases (c) AIFIVE-1-Ni
 424 crystalline structure in which yellow polyhedra donates AlF_5^{2-} pillar, whereas other atoms were shown in CPK
 425 coloring scheme (d), Column breakthrough tests through gas mixture with composition (5/5/90) for $\text{CO}_2/\text{H}_2\text{S}/\text{CH}_4$
 426 with the flowrate of $10 \text{ cm}^3 \cdot \text{min}^{-1}$ with the flowrate of $10 \text{ cm}^3 \cdot \text{min}^{-1}$ on NbOFFIVE-1-Ni at 25°C and 50°C (1 bar),
 427 referring to the influence of different adsorption temperature against response time of various gases. Reprinted from
 428 Ref.¹²² Copyright 2018, Nature Energy (e) Synthesis route of various TKL MOFs (f) The isotherms of CO_2 adsorption
 429 for various TKL MOFs at low pressure and 273 K. Reprinted from Ref.¹²⁴ Copyright 2013, Nature Scientific Reports.

430 It is particularly important to note that MOFs adsorb CO_2 very efficiently because of the small
 431 amount of water vapor in the flue gases.¹²⁵ According to Taddei et al.¹²⁶ gas adsorption
 432 technology plays a crucial role in improving MOF's stability under humid conditions. The relative
 433 humidity behavior of MOF namely MIL-100(Fe) was first investigated by Llewellyn et al.⁷³
 434 which exhibited a CO_2 capacity rise from $0.59\text{-}2.38 \text{ mmol} \cdot \text{g}^{-1}$ with a relative humidity rise from
 435 (3%-40%) at a partial pressure of 0.2 bar of CO_2 .¹²⁷ Fracaroli et al.¹²⁸ utilized IRMOF-74-III-

436 CH₂NH₂ for the selective absorption of CO₂ at a relative humidity of 65%. The experimental
437 results revealed that this MOF showed effective performance for CO₂ absorption to about 3.2
438 mmol.g⁻¹ at 1 bar).¹²⁸

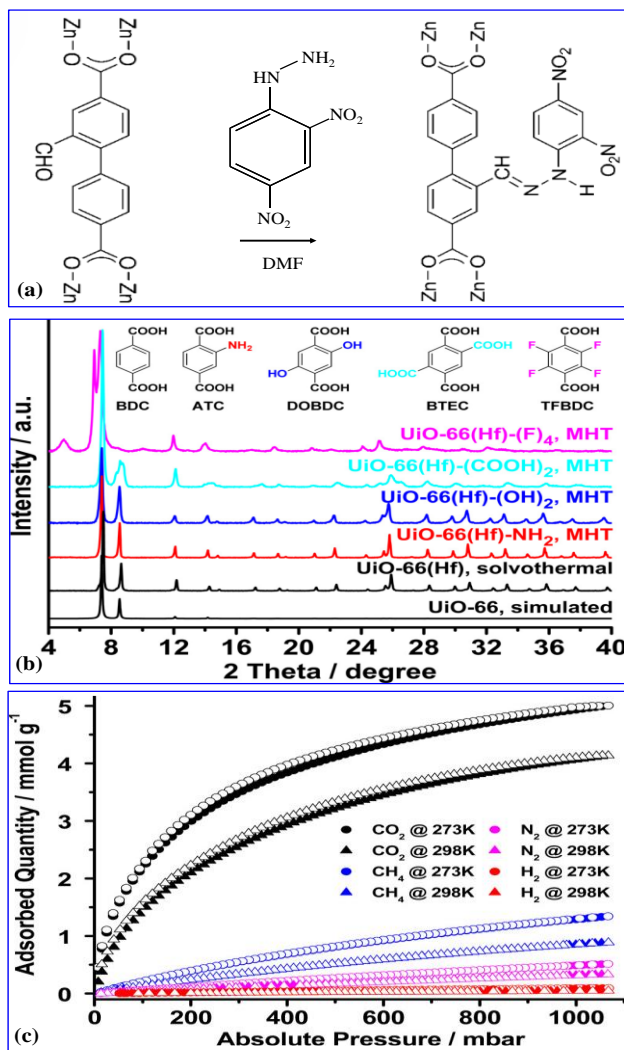
439 During post-synthesis functionalization, the pre-synthesized framework is chemically modified
440 with the functional groups.¹²⁹ As a result of the reaction between pendant aldehydes, azidoes, and
441 pendant amines, new chemical functionalities are synthesized that cannot be produced directly
442 under the process of solvothermal or hydrothermal reactions, as well as the activation of pre-
443 existing catalytic sites. Several goals could be achieved through the use of PSM.³⁶ (A) Functional
444 groups could be introduced into MOFs with PSM. (B) Coordination polymer networks can be
445 modified and exchanged by modifying organic linkers. (C) Cation exchange between MOFs. The
446 techniques help to make MOF networks more desirable.¹³⁰

447 Through the impregnation of polyethyleneimine (PEI) into MIL-101, Bhattacharjee et al.¹³¹
448 synthesized an amine-functionalized MOF. During the final application of the compound at 0.15
449 bar and 298 K with loadings of 100 wt% PEI, the results exhibited that the material showed a
450 significant increase in the amount of CO₂ that could be adsorbed at low pressures (4.20 mmol.g⁻¹
451 at 298 K, 0.15 bar), and showed high selectivity for CO₂ over N₂ in the flue gas (1200 at 323 K
452 and 770 at 298 K). In addition, dual amine functionalized MIL-101 is synthesized by adding PEI
453 directly into the "amine-functionalized MIL-101" to produce a product with increased CO₂
454 adsorption capacities, and CO₂/CH₄ selectivity at low pressures.¹³¹ One example of en-grafted
455 MOF is en-MOF-74, which has been specifically designed with an amine loading of 16.7 wt.%.
456 When this modified MOF is exposed to a pressure value of 0.15 bar and a temperature value of
457 298 K, it exhibits a remarkable uptake of CO₂ (13.7 wt. %).¹³² There is another study conducted
458 by Gaikwad et al.¹³³ in which the effects of amine functionalization on MOF-177 CO₂ adsorption
459 capacity have been studied at different temperatures, such as 298 to 328 K. In comparison with
460 the parent MOF-177, the amine-functionalized MOF-177 was shown to have CO₂ adsorption
461 capacity of 4.6 mmol.g⁻¹ at 328 K.¹³³

462 By reacting 2,4-dinitrophenylhydrazine with pendant aldehyde, Burrows et al.¹³⁴ synthesized the
463 hydrazone from a functionalized MOF with the formula [Zn₄O(bpdc)₃]_n (IRMOF-9) as shown in
464 **Fig 7a**. They reported that their results have strong implications for MOF as catalyst supports
465 since molecular doping allows for control of catalyst loading. Thompson et al.¹³⁵ synthesized a

466 new mixed-linker ZIF involving a functional group aldehyde and then modified it by adding
467 ethylenediamine as a linker into the framework. The results of gas permeation showed that tuning
468 the surface properties of ZIF-8 via post-synthesis modification or through mixed linker
469 modifications the successful improvement in selectivity for CO₂/CH₄ observed as compared with
470 ordinary ZIF-8 to make them commercially available adsorbents which increases their heat of
471 adsorption for CO₂ without any deformation in structural properties.¹³⁵

472 In functionalized MOFs, strong bonds are formed between gas molecules and MOFs, which
473 makes it difficult to regenerate the MOFs. “Solvent-aided ligand inclusion” (SALI) is a new
474 functionalization technique to resolve this problem. Fluorinated chains were fixed to zirconium
475 secondary basic units in NU-1000. Higher absorption values of CO₂ than parent NU-1000 were
476 possibly created by the development of attractive interactions between the linkers group COOH
477 and OH this is due to the attraction of the C and CO₂ molecule quadrupole moment. Additionally,
478 “solvothermal methods” are used to synthesize hafnium-based MOFs, such as UiO-66(Hf) MOFs,
479 to perform better gas adsorption.¹³⁶ **Fig 7b.** shows the PXRD of UiO-66(Hf)-type MOFs. They
480 reported that among all the produced MOFs, UiO-66(Hf)-(OH)₂ demonstrates the greatest CO₂
481 adsorption gravimetrically, measuring 1.81 mmol.g⁻¹ at temperature 298 K and pressure 0.15 bar.
482 This is 400% greater than UiO-66(Hf), which only reaches 0.36 mmol.g⁻¹ and presents 4.06
483 mmol.g⁻¹ at pressure 1 bar and temperature 298 K. Additionally, UiO66(Hf)-NH₂ has 0.93
484 mmol.g⁻¹ of the second-largest capacity of CO₂ absorption; as a result, UiO-66(Hf)-(COOH)₂
485 presented 0.40 mmol.g⁻¹ of the capacity to absorb CO₂ followed by UiO-66(Hf)- (OH)₂ displays
486 0.28 mmol.g⁻¹ of CO₂ adsorption as shown in **Fig 7c.**¹³⁷

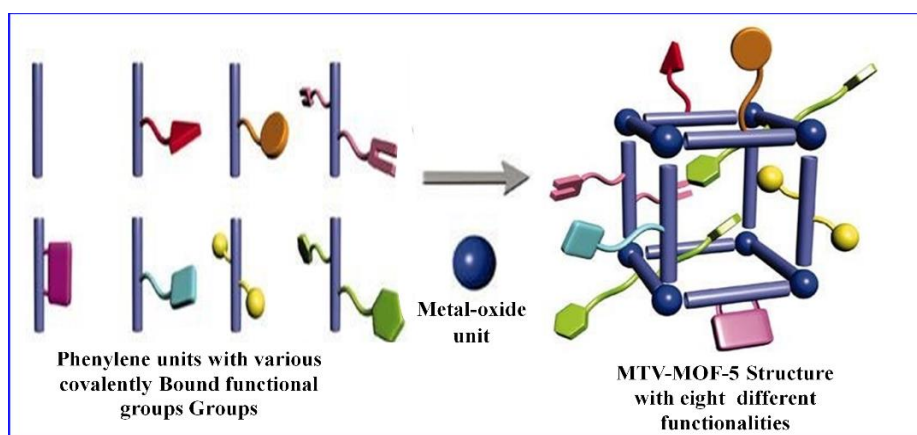


487
 488 **Fig 7. a)** Pendant aldehyde groups in reaction with hydrazine through Post-synthesis modification. Reprinted from
 489 Ref.¹³⁴ Copyright 2008, John Wiley & Sons, Inc **b)** comparison of crystallinity for various UiO-66(Hf)-type MOFs **c)**
 490 The isotherms of gas adsorption for UiO-66(Hf)-(OH)₂. Reprinted from Ref.¹³⁷ Copyright 2016, American Chemical
 491 Society

492 MOFs containing dual alkyl ether side chains as linkers are recognized for their structural
 493 flexibility owing to the solvent-like characteristics of ether functional moieties. Schmid et al.¹³⁸
 494 reported an unusual structural flexibility and gas uptake by IRMOF-1, MOF-5, and
 495 [Zn₂(BDC)₂(dabco)]_n, having additional alkyl ether groups. The addition of a functional group
 496 capable of forming hydrogen bonds, such as alcohol, to the organic ligands in MIL-53(Al)-type
 497 materials can lead to the generation of flexible frameworks. For example, Sah et al.¹³⁹ synthesized
 498 robust and flexible MIL-53(Al)-type MOFs showing a breathing mechanism that can be
 499 manipulated by systematically adding hydrogen bonding sites within their framework.
 500 Incorporating 2-hydroxy terephthalate and 2,5-dihydroxy terephthalate organic ligands led to the

501 production of MIL-53(Al)-OH and MIL-53(Al)-(OH)₂ respectively. The optimized crystal
502 structures of alcohol-functionalized MIL-53(Al) MOFs were calculated using a density functional
503 tight binding approach. Hong et al.¹⁴⁰ reported the synthesis of a thiol-functionalized framework,
504 termed UiO-66-(SH)₂. In this study, the thiol groups within the MOF structure were oxidized
505 using H₂O₂ and followed by treatment with an H₂SO₄ solution. This process resulted in the
506 formation of a modified product called UiO-66-(SO₃H)₂, containing sulfonic acid (SO₃H) groups.
507 It is noteworthy that the presence of sulfonate groups could hinder MOF formation due to their
508 ability to coordinate with metals. As a result, this PSM approach, involving the introduction of
509 thiol groups followed by oxidation, was identified as the most effective method for introducing
510 sulfonates into MOFs. The incorporation of carboxylic acids and their derivatives into MOF
511 ligands poses challenges due to metal-carboxylate interactions being the main interactions in
512 MOF formation. **Table 6.** shows the CO₂ adsorption performance of different MOFs modified
513 with different functional groups at different pressures and temperatures. Therefore, the literature
514 contains only a limited number of examples showcasing MOFs featuring carboxylic acid
515 functionality. In 2019, Liu's research group post-synthetically modified a Zr-based MOF known
516 as PCN-700 by introducing a ligand with carboxylic acid functionality. Specifically, they
517 introduced both a basic functional group (BDC-NH₂) and an acidic functional group (TPDC-
518 (COOH)₂) into PCN-700. The PCN-700 MOFs possess two distinct types of pockets in their
519 structure with different ligand lengths, allowing the NH₂-functionalized BDC and COOH-
520 functionalized TPDC ligands to fit snugly into each pore type.¹⁴¹ Subsequently, a two-step process
521 involving deacetalization followed by Knoevenagel condensation was carried out using this dually
522 functionalized PCN-700 MOF. The deacetalization step was facilitated by the acidic component
523 (COOH) of the MOF, while the basic site (NH₂) efficiently catalyzed the Knoevenagel
524 condensation reaction.¹⁴² Deng et al.¹ in their study showed that MOFs can be incorporated with a
525 large number of different functionalities on linking groups. They made complex MOFs from 1,4-
526 benzenedicarboxylate (denoted by A) and its derivatives -*NH₂, -Br, -(Cl)₂, -NO₂, -(CH₃)₂, -C₄H₄,
527 -(OC₃H₅)₂, and -(OC₇H₇)₂ (denoted by B to I, respectively) to synthesize 18 multivariate (MTV)
528 MOF-5 type structures that contain up to eight distinct functionalities in one phase. They observed
529 that the complex arrangements of several functional groups within the pores can lead to properties
530 that are not simply linear sums of those of the pure components. For example, a member of this
531 series, MTV-MOF-5-EHI, demonstrated up to 400% better selectivity for CO₂ over CO compared

532 with its best same counterparts. The following **Fig 8.** shows the different functional groups
 533 attached to the structure of MTV-MOF-5.



534

535 **Fig 8.** Representation of MTV-MOF-5 structures with up to eight different functionalities distributed in
 536 one crystalline material. Reproduced from Ref.¹ Copyright 2010, American Association for the
 537 Advancement of Science.

538 **Table 6.** CO₂ adsorption performance of different functionalized MOFs at different pressure and temperatures.

MOF	Functional group	Pressure (bar)	Temperature (K)	CO ₂ adsorption (mmol g ⁻¹)	Ref.
MFM-188	Amide	1	298	5.35	143
HHU-2	Amide	1	298	4.80	144
TEPA-MOF-177	Amine	1	328	4.6	133
Fe-ZIF-8-NH ₂	Amine	1	273	2.81	145
LMOF-202	Carbonyl	1	195	6.24	146
Cu-MOF 1	Carbonyl	1	298	4.96	147
Zn-MOF-Crown	Ether	1	298	2.62	148
[Zn(odip) _{0.5} (bpe) _{0.5} (CH ₃ OH)·0.5NMF.H ₂ O	Ether	1	313	5.29	149
[Zn ₉ (OH) ₂ L ₆](H ₃ O) ₂ (H ₂ O) ₆	Hydroxy	1	273	2.27	150
HHU-4	Hydroxy	1	273	7.35	151
IISERP-MOF-20	Imidazole	1	298	3.5	152
{[CO ₂ L ₂ (TPA) ₂]·12H ₂ O} _n	Imidazole	1	273	3.12	153
IPM-MOF-110	Imide	0.2	298	2.39	154
Zn(NDC)(DPMBI)	Imide	1	298	2.74	155
ZU-301	oxalate	1	323	2.27	156
ZnAtzOx	oxalate	1	293	3.8	157
MIL-91(Al)	Phosphonate	1	303	2.6	158
[Ni _{1.5} (4,4-bipy)1.5(H ₃ L)(H ₂ O) ₃][H ₂ O] ₇	Phosphonate	1	303	0.4	159
[Zn ₂ (btac)(btzmb)] _n ·8nH ₂ O	Pyridinium	1	298	4.37	160
UiO-67-bpy-Me	Pyridinium	0.85	273	3.39	161
USTC-253-TFA	Sulfonate	1	298	2.13	162

PPN-6-SO ₃ H	Sulfonate	1	295	3.60	163
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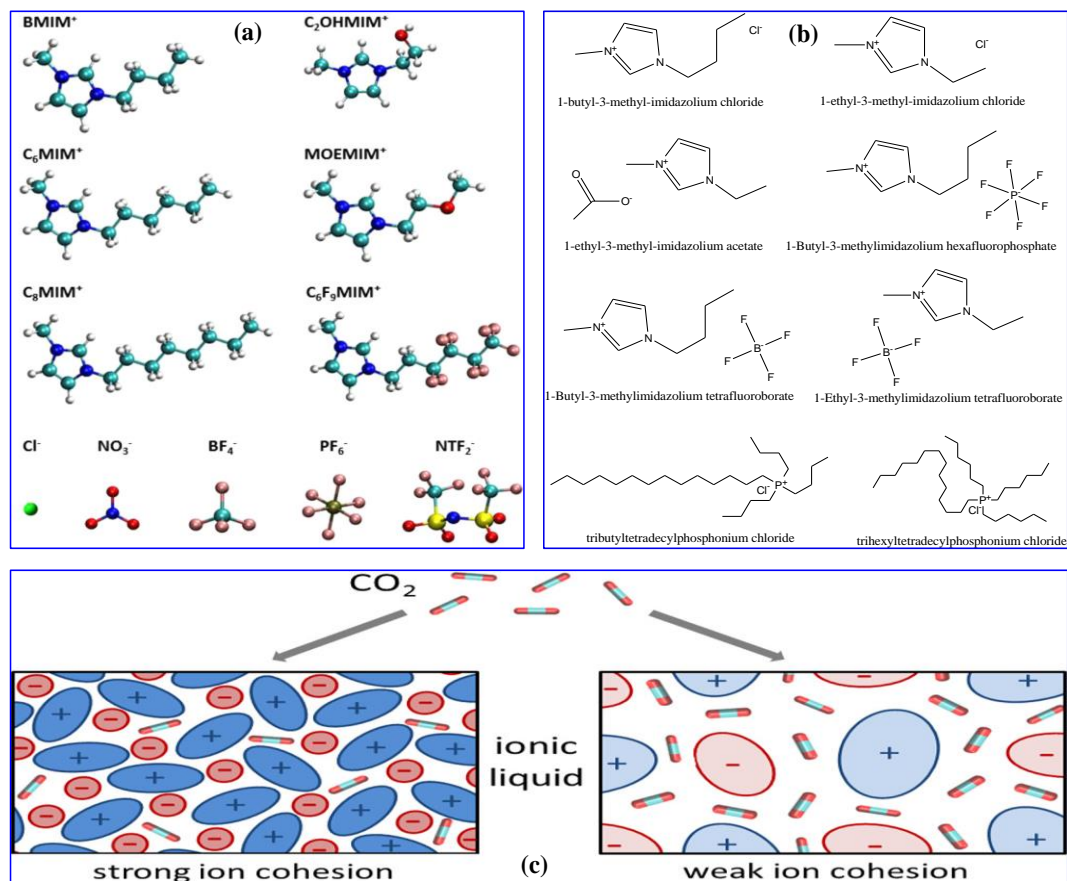
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540 3. Ionic Liquids

541 ILs are magical solvents with the unique features of non-volatility, recyclability, and excellent
 542 thermal stability along with a wide range of tunability in the selection of various cations and
 543 anions.²⁴ ILs are composed of the bulky organic cation having low molecular symmetry and the
 544 small organic/inorganic anion moieties which are in the molten form in their pure state.^{164,165} The
 545 nature of high absorption capacity, biodegradability, and less corrosivity associated with ILs
 546 makes them enables to be applied as a replacement solvent in place of existing volatile, corrosive
 547 and degradation-originated amine-based solvents.^{166,167} The unique chemical and physical
 548 characteristics of ILs provided them more opportunities to be utilized in numerous applications
 549 like catalysis, energy storage, electrochemistry, separation, and other applications. Moreover, the
 550 nature of high inflammability and high affinity towards CO₂ makes them enables to be utilized for
 551 gas separation applications for carbon capture.¹⁶⁸

552 3.1. CO₂ absorption in ILs

553 CO₂ is absorbed by the ILs under the influence of physical interactions between the anions and
 554 cations of the ILs with CO₂ molecules. Therefore, it can be said that the degree of CO₂ solubility
 555 in ILs is determined by the types of anions and cations present.¹⁶⁴ In contrast to the cations present
 556 in ILs, anions are considered to have a greater impact on the absorption of CO₂.¹⁶⁹ **Fig 9a** lists
 557 some cations and anions commonly used to capture CO₂. Cadena et al.¹⁷⁰ did experimentation to
 558 investigate the solubility behavior of CO₂ in ILs and found that anions contribute more
 559 significantly to CO₂ solubility than their anions counterparts. Liu et al.¹⁷¹ performed a simulation-
 560 based study to examine the diffusivity, solubility, and permeability of CO₂ using three different
 561 ILs having the same cation and different anions. The selected three ILs were [Emim][NTf₂],
 562 [Emim][B(CN)₄], and [Emim][BF₄]. Simulation results agree satisfactorily results with the
 563 experiment in terms of [Emim][B(CN)₄] > [Emim][NTf₂] > [Emim][BF₄]. The high CO₂
 564 solubility in [Emim][B(CN)₄] is attributable to a weaker interaction between anion and cation, a
 565 higher fraction of larger cavities, a greater free volume, and good interaction with CO₂.¹⁷¹ **Fig 9b**
 566 shows the CO₂ absorption mechanism in ILs. The chemical structures of various ILs used for CO₂
 567 capture are shown in **Fig 9c**.



568

569 **Fig 9.** a) Structure of various cations and anions constituting ILs. b) Structure of different ILs used in CO₂ capture c)
 570 Schematic illustration of CO₂ absorption mechanism in ILs. Reprinted from Ref.¹⁷² Copyright 2015, American
 571 Chemical Society.

572 In one of the studies by Hou et al.¹⁷³ the effects of having the same anion under different cations
 573 were investigated using [NTf₂]⁻ and [BF₄]⁻ as anions with several different cations of [Pmmim]⁺,
 574 [Bmim]⁺, [Bmpy]⁺ and [perfluoro-Hmim] under the temperatures range from 10-50°C. As a result
 575 of the experiments, they found that the contribution of different cations slightly affected the
 576 solubility of CO₂. However [NTf₂]⁻ anion shows higher solubility for CO₂ as compared with
 577 adding [BF₄]⁻.¹⁷³ In an experimental study by Anthony et al.¹⁶⁹ the effects of adding different
 578 cations (ammonium, imidazolium, phosphonium, and pyrrolidinium), in combination with anions
 579 [NTf₂]⁻, [PF₆]⁻ and [BF₄]⁻) was investigated. It was found that [NTf₂]⁻ anion in ILs showed a
 580 higher gas solubility as compared with the [PF₆]⁻ anions, which implies that the anion species
 581 have a central role in the ILs to enhance the CO₂ solubility.¹⁶⁹ **Table 7.** shows the CO₂ solubility
 582 of phosphonium⁻, imidazolium⁻, pyridinium⁻, and pyrrolidinium⁻ based IL.¹⁷⁴ In one of the
 583 investigations by Noorani et al.¹⁷⁵ the CO₂ solubility was tested in the series of 1-alkyl-3-methyl

584 imidazolium and 1-alkyl-4-methyl pyridinium-based ILs under the influence of increasing the
 585 cationic alkyl chain length with various anions of thiocyanate ([SCN]⁻, chloride [Cl]⁻ and bromide
 586 [Br]⁻. Although cations only contribute to a small proportion of CO₂ solubility, their effects are
 587 still significant enough to make them worth considering. However, the presence of long alkyl
 588 chains, fluorination, and modification with ester groups on cations along with the same anions
 589 shows significant effects on improving CO₂ solubility. They experienced that cationic alkyl chain
 590 length and type of anions are the major key contributors to enhancing the CO₂ solubility of ILs.
 591 They concluded that CO₂ solubility increased in both 1-alkyl-3-methylimidazolium and 1-alkyl-4-
 592 methyl pyridinium-based ILs increase with increase the cationic alkyl chain length and following
 593 the anionic order: [SCN]⁻ > [Cl]⁻ > [Br]⁻.¹⁷⁵

594 **Table 7.** CO₂ solubility in different classes of ILs

Type	Ionic liquid	Pressure (bar)	Temperature (K)	Solubility (CO ₂ /mol-IL)	Ref
Imidazolium	[Emim][NTf ₂]	10	303	0.225	176
			333	0.144	
	[Emim][Ac]	19.9	298	0.428	177
	[Emim][tfa]	19.9		0.282	
	[Emim][EtSO ₄]	94.6	333	0.457	178
	[Bmim][NO ₃]	92.6	323	0.530	
	[Bmim][PF ₆]	96.6	313	0.729	
	[Emim][NTf ₂]	9.03	298	0.209	179
	[Emim][BF ₄]	8.7		0.106	
Pyridinium	[N-BuPy][BF ₄]	92.3	323	0.581	178
				0.200	181
	[HmPy][NTf ₂]	1-10	283	0.200	181
				0.879	182
	[thtdp][NTf ₂]	721	296	0.879	182
				0.308	
		1.06	293	0.879	
	[MeBuPy][BF ₄]	10	303	0.144	176
	[MeBuPy][N(CN) ₂]			0.096	
[MeBuPy][SCN]			0.061		
Pyrrolidinium	[MeBuPyr][SCN]	10	303	0.097	176
				0.120	
	[MeBuPyr][N(CN) ₂]			0.167	
	[MeBuPyr][tfa]			0.167	
[BmPyr][fep]	18	283	0.498	183	
Phosphonium	[thtdp][Cl]	149	302	0.800	176,182
				0.200	
	[thtdp][NTf ₂]	721.8	296	0.879	176,182
				0.308	
		1.06	293	0.879	
[tbp][for]	19.9	298	0.348	177	

595

596 3.2. Functionalization of ILs to Capture CO₂

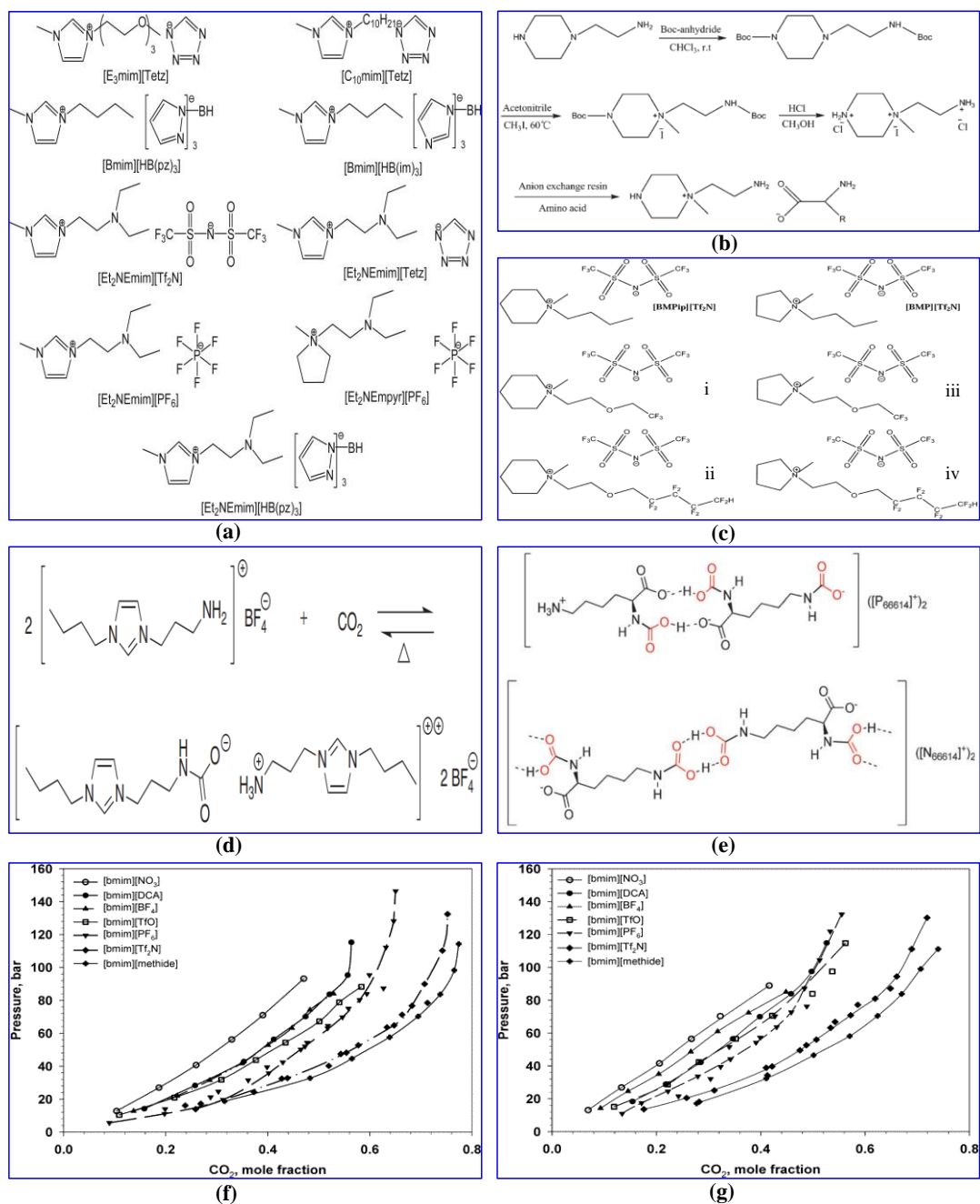
597 When compared to traditional solvents, the physisorption of ILs results in minimum CO₂
598 absorption at low-pressure post-combustion conditions.¹⁸⁴ CO₂ absorption of ILs can be improved
599 by chemisorption through introducing CO₂-philic functional groups (amine, carbonyl, and Fluro)
600 with the cation/anions.¹⁸⁵ Functionalized ILs appear to have stronger absorption ability under low-
601 pressure conditions than traditional ILs, which has the benefit of improving their performance
602 under harsh conditions.¹⁸⁶ **Fig 10a** shows the structures of different imidazolium-based
603 functionalized ILs.

604 The amine groups functionalized ILs have revealed significant concern in enhancing absorbent
605 reactivity and affinity towards CO₂ molecule solubility.¹⁸⁷ Generally, for CO₂ capture, there are
606 two types of amine-functionalized ILs: one is cation-functionalized ILs and the other is anion-
607 functionalized ILs.¹⁸⁸ Bates et al.¹⁸⁹ discovered an increasing trend for CO₂ solubility by attaching
608 an amine-functional group with imidazolium cation. **Fig 10b** shows the synthesis route of amine-
609 based ILs and **Fig 10c) i, ii, iii, and iv**, show piperidinium and pyrrolidinium-based ILs with the
610 fluorinated chain attached to the cation. The high solubility for CO₂ is referred to as the high
611 basicity associated with the amine group. Due to the acidic nature of CO₂, the interaction between
612 amine groups and CO₂ is stronger which promotes its high solubility with the basicity of ILs.¹⁸⁹
613 **Fig 10d.** shows the phenomena of CO₂ chemisorption associated with amino-functionalized IL.
614 Saravana et al.¹⁹⁰ investigated the influence of adding cations on CO₂ absorption by replacing
615 [P₆₆₆₁₄] cation with [N₆₆₆₁₄]. They observed CO₂ absorption for [N₆₆₆₁₄] cation with different
616 anions such as histidine [His], lysine [Lys], and glutamine [Gln]. They reported the high
617 absorption capacity of 2.1 mol CO₂ per mol of IL for lysine[Lys] based IL which emphasizes the
618 importance of adding anion to enhance the CO₂ absorption. Both the [N₆₆₆₁₄][Lys]-CO₂ and
619 [P₆₆₆₁₄] [Lys]-CO₂ were constituted of two separate anion structures shown in **Fig 10e.**¹⁹⁰

620 Kanakubo et al.¹⁹¹ performed X-ray diffraction studies and found that anions appear to play the
621 most essential role in CO₂ solubilization. Noorani et al.¹⁹² investigated the phenomena of CO₂
622 absorption using AAILs having imidazolium cation and various aminate (alanine, glycine, and
623 valine) and found that glycinate anion exhibited the maximum CO₂ absorption capacity of about
624 (mCO₂/mol.kg⁻¹=10.42) than alanine (4.45) and valine (3.901) at 4 bar and 288K, respectively.¹⁹²
625 In another study by Noorani et al.¹⁹³ the effect of adding anion on CO₂ absorption was examined
626 using cation [B4MePyr] with various anions (glycinate [Gly], alaninate [Ala], valinate [Val],

627 proline [L-Pro], tyrosinate [Tyr], histidine [His], Lysinate [Lys], and arginate [Arg]) upto feed
628 pressure of 6 bar and 298.15 K. Because of their fundamental nature and polar side chains, [Arg],
629 [Lys], and [His] have maximum CO₂ absorption than [B4MePyr][AA]s. This aspect could be
630 attributed to stronger interactions among acid and base in these ILs compared to others
631 [B4MePyr] [AA]s. [Lys] and [Arg] absorb more CO₂ than [His], [Ala], [Pro], [Val], and [Gly],
632 with 0.612 and 0.551 mol/mol, respectively.¹⁹³ **Table 8.** shows the CO₂ solubility of various
633 functionalized ILs at various pressures and temperatures.

634 The carbonate and carbamate production pathways for CO₂ absorption are used by primary,
635 secondary, and tertiary amine groups. Primary amine functionalized ILs absorb CO₂ by creating a
636 particular set of carbamate salts, whereas adding an amine functional group to IL's cation
637 increases carbamate formation. Sanchez et al.¹⁹⁴ studied the impact of amine-functionalization
638 on imidazolium cation and discovered that primary amine-functionalized ILs have maximum CO₂
639 solubility than tertiary amine-functionalized and non-functionalized ILs.¹⁹⁴



640

641 **Fig 10 a** The structures of [E₃mim][Tetz], [C₁₀mim][Tetz], [Bmim][HB(pz)₃], [Bmim][HB(im)₃], [Et₂NEmim][
 642 NTf₂], [Et₂NEmim][Tetz], [Et₂NEmim][PF₆], [Et₂NEmpyr][PF₆] and [Et₂NEmim][HB(pz)₃]. Reprinted from Ref.⁹
 643 Copyright 2015, Elsevier. and from Ref.¹⁹⁵ Copyright 2018, Elsevier. **b** Synthetic route of 1-(2-aminoethyl)-1-
 644 methylpiperazin-1-ium amino acid ILs ([AEMP][A]⁻). [A]⁻ = [Gly]⁻, [Ala]⁻, [Pro]⁻, [Leu]⁻. Reprinted from Ref.¹⁹⁶
 645 Copyright 2013, Royal Society of Chemistry **c** **i and ii**, Piperidinium-based ionic liquids with the fluorinated chain
 646 attached to the cation. **iii and iv**, Pyrrolidinium-based ionic liquids with the fluorinated chain attached to the cation.
 647 Reprinted from Ref.¹⁹⁷ Copyright 2018, Royal Society of Chemistry. **d** Chemisorption mechanism by IL amino group
 648 functionalized ILs. Reprinted from Ref.¹⁹⁸ Copyright 2004, American Chemical Society. **e** The structures suggested
 649 the inclusion of anions in the [P₆₆₆₁₄]⁺ and [N₆₆₆₁₄]⁺. Reprinted from Ref.¹⁹⁰ Copyright 2014, John Wiley &

650 Sons Inc **f)** Influence of various anions on CO₂ solubility with [bmim] cation at 25 °C **g)** Influence of various anions
 651 on CO₂ solubility with [bmim] cation at 40°C. Reprinted from Ref.¹⁹⁹ Copyright 2020, Elsevier.

652 **Table 8.** CO₂ solubility of various functionalized ILs at different pressure and temperature.

Functionalized ILs	Mw (g mol ⁻¹)	Pressure (bar)	Temperature (K)	CO ₂ solubility (mol kg ⁻¹)	Ref
[Bmim][NTf ₂]	404.33	9.5	313.2–353.2	0.27–3.88	200
[Emim][ATZ]	194.24	1	298.15	0.67	201
[Emim][N(CN) ₂]	177.21	0.5–3	298.2–373.2	0.0096–0.17	202
[Emim][TCM]	201.23	0.5–3	298.2–373.2	5–16.1	202
[Bmim][OTf]	288.29	32.367	303.15–353.15	0–2.48	203
[Hmim][NTf ₂]	447.42	35.555	303.15–353.15	0–2.65	203
[Bmim][BF ₄]	226.02	0.28–34.38	273.15–353.15	2.49–4.2	204
[DEA][Bu]	161.29	7.25–200	303–333	0.63–3.71	205
[N ₁₁₁₄][NTf ₂]	396.37	0.6–9.95	298	0.004–0.61	206
[Emim][AC]	170.20	0.6–9.94	298	0.0043–0.78	206
[PMPy][N(CN) ₂]	194.23	0.6–9.94	298	0.0044–0.71	206
[DMAPAH][EOAc]	---	1	303.2	2.44	207
[DEEDAH][EOAc]	---	1	303.2	1.28	207
[DMEDAH][EOAc]	---	1	303.2	2.32	207
[Emim][AC]	170.2	1	313.2	1.65	208
[Emim][Ala]	200.26	1	313.2	1.89	208
[Emim][Gly]	186.3	1	313.2	2.32	208
[TETAH][Lys]	266.43	1	313.15	9.72	209
[DETAH][Lys]	277.39	1	313.15	7.68	209
[DETAH][Gly]	178.24	1	313.15	10.15	210
[DETAH][Tz]	172.23	1	313.15	10.1	210
[DETAH][Py]	171.25	1	313.15	11.91	210
[DETAH][Im]	171.25	1	313.15	11.39	210
[N ₁₁₁₄][Lys]	219	1	303	1.84	211
[Cho][Ser]	---	1.5	303.15	0.89	212
[Cho][Pro]	---	1.5	303.15	0.94	212
[Cho][Gly]	---	1	303.15	0.96	212
[Cho][Lys]	---	1.7	303.15	1.29	212
[Hmim][B(CN) ₄]	282.2	1	298.15	0.52	213
[Bmim][N(CN) ₂]	205.3	1	298.15	0.38	213
[Bmim][TCM]	229.3	1	298.15	0.42	213
[Emim][N(CN) ₂]	177.2	1	298.15	0.375	213
[Bmim][SCN]	197.3	1	298.15	0.269	213
[Bmim][NTf ₂]	419.4	1	298.15	0.087	213
[Emim][NTf ₂]	391.3	1	298.15	0.083	213
[NEMH][Ac]	175.23	5	298.15	0.74	214
[NEMH][Pro]	189.26	5	298.15	0.69	214
[TEAH][Pro]	175.27	5	298.15	0.67	214

653 Ether functionalities also improve oxygen interaction with the carbon of CO₂ and free volume
 654 which results in high CO₂ solubility.²¹⁵ According to Lin et al.²¹⁶ and Shannon et al.²¹⁷ the
 655 inclusion of polar groups such as ether has a great influence on CO₂/CH₄ separation. Zhang et
 656 al.²¹⁸ observed that repulsion between polar groups such as ether and nonpolar gases like CH₄ was
 657 remarkably useful for efficient CO₂ separation in ether-functionalized pyridinium ILs. These
 658 findings are significant for ILs that could be employed as selective CO₂ absorbents.²¹⁸ Zhou et

659 al.²¹⁹ characterized two types of ether-functionalized imidazolium ILs, [EOMmim][PF₆]
660 and [EOMmim][NTf₂]. They found that the inclusion of ether groups on cation significantly
661 improved the CO₂ solubility and CO₂/N₂, and CO₂/O₂ selectivity.²¹⁹

662 High electronegativity of fluorine atom than hydrogen atom results in weak Lewis's base
663 formation which can make a polar bond with the carbon atom of the CO₂ molecule. Anions with
664 fluor groups have higher CO₂ affinity and the maximum number of fluoro groups on an anion
665 enhances its CO₂ solubility.²²⁰ As a result, fluorine-substituted IL and side chain length provide
666 large free space for absorbing more CO₂ molecules and making stronger connections between
667 fluorinated alkyl chains and CO₂.²²¹ Aki et al.¹⁹⁸ studied the effect of fluorination on CO₂
668 solubility using 1-butyl-3-methylimidazolium ([bmim]) as a cation with various anions such as
669 [PF₆],[NO₃],[N(CN)₂],[BF₄],[TfO],[NTf₂], and [methide]. **Fig 10f** shows the influence of various
670 anions on CO₂ solubility at 25°C which revealed that anion fluorination has a considerable impact
671 on CO₂ solubility. CO₂ has a lower solubility with non-fluorinated anions [NO₃] and [N(CN)₂],
672 whereas IL with fluoroalkyl group anion [TfO], [NTf₂], and methide has a high CO₂ solubility
673 which may be due to a stable interaction between CO₂ and fluoroalkyl substitution on the
674 anion. The CO₂ solubility increases with the rise in the CF₃ group in the anion. At 25°C the CO₂
675 solubility in [Bmim] cation-based ILs follows the increasing order of [NO₃]<[N(CN)₂]
676 [BF₄]<[PF₆]<[TfO]<[NTf₂]<[methide].¹⁹⁸ Anderson and co-workers were the first to explore this
677 approach of increasing CO₂ solubility in ILs. The authors give an in-detail review of gas solubility
678 in ILs to present that the fluorination of the cation enhances CO₂ solubility on a pTx diagram,
679 although this impact appears to decrease as the fluorinated chain length increases.¹⁸¹ Aki et al.¹⁹⁸
680 also explored how cation affects CO₂ solubility. Three ILs were selected, under the influence of
681 the same anion [NTf₂] and different imidazolium-based cations exposed with different alkyl chain
682 lengths namely [Omim], [Hmim], and 2,3-dimethyl-1-hexylimidazolium [Omim] [Hmim]. The
683 absorption of CO₂ in these ILs was measured at 25, 40, and 60°C as illustrated in **Fig 10g** for
684 40°C.¹⁹⁸ According to Almantariotis et al.²²² the CO₂ solubility in fluorine-substituted IL
685 [C₈H₄F₁₃mim] [NTf₂] was observed to be greater than [Omim][NTf₂]. The primary reason for
686 this is increasing side chain length and fluorination on IL subjected to a larger free area to absorb
687 CO₂. Moreover, the stronger interaction b/w fluorinated alkyl chains and CO₂, are promising
688 factors for the physical dissolution of CO₂ in ILs.²²²

689 Carbonyl groups are commonly used in ILs to increase CO₂ solubility. Carbonyl functional groups
690 can operate as Lewis acid by interacting with electron-deficient carbon of CO₂ molecule,
691 however, oxygen atoms can serve as Lewis base and form a C-H...O hydrogen bond. According to
692 different studies, adding carbonyl groups to the anion, such as acetate and aldehyde, is the most
693 effective method for enhancing CO₂ phillicity in ILs.¹⁷⁹ Shiflett et al.²²³ and Gomez-Coma et al.²²⁴
694 examined that ILs having acetate anion, [CH₃-COO]⁻, show a reactive absorption for CO₂ capture.
695 Functional groups like CH₂CH₂C=OCH₃, C(CH₃)₃, CH₃CH₂, and CH₃ form effective
696 combinations with CO₂ molecules, resulting in strong chemisorption. Carbonyl functional groups
697 can also be fluorinated to increase CO₂-phillicity. Substituting carbon atoms adjacent to functional
698 groups with electronegative fluorine atoms reduces electron density, making carbonyl groups
699 weaker Lewis bases.²²⁵

700 **4. MOFs-ILs systems: Synthesis strategies**

701 Integrating MOFs and ILs into composites is one of the most encouraging strategies for increasing
702 the selectivity of material towards targeted gas molecules by providing strong adsorption sites.
703 The tunable nature of ILs, along with the advantage of good porosity and higher specific surface
704 area of MOFs make them a favorable candidate for efficient gas separation.²²⁶ The integration of
705 ILs into MOFs can be classified into two types of approaches used for the synthesis of MOF-IL
706 composites: one is iono-thermal synthesis and the other one is a post-synthesis modification.²²⁷

707 **4.1. Iono-thermal synthesis**

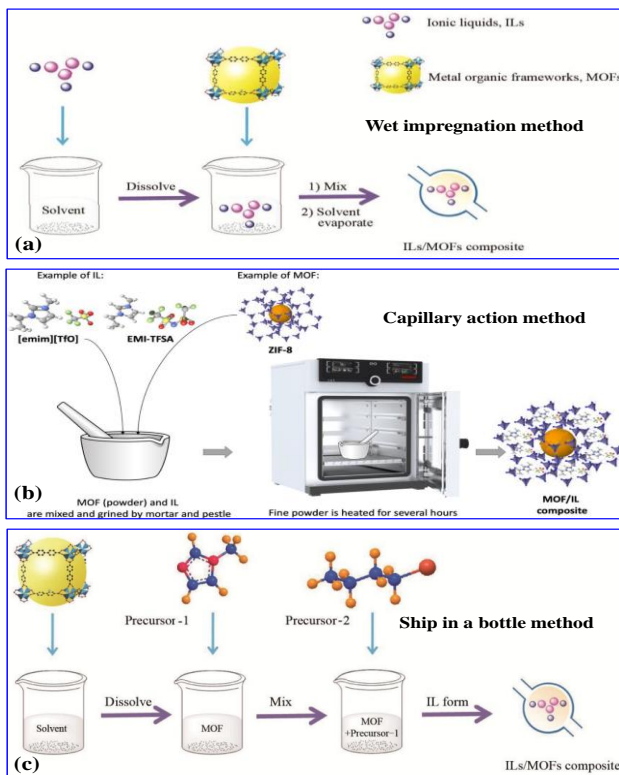
708 The iono-thermal synthesis of MOF-IL composites involves ILs as a solvent or structure-directing
709 agent in the synthesis of composite materials.²²⁷ The first step in the process is to dissolve
710 precursors of MOF and IL into each other, and then the solution was placed in a stainless-steel
711 autoclave. Afterward, the solution is placed in a furnace for a couple of days for its treatment at a
712 specified temperature to obtain the desired results. Lastly, the solution is allowed to cool down to
713 ambient temperature, which allows crystals to form. A major characteristic of iono-thermal MOFs
714 is that the frameworks are mostly made up of cation parts of ILs.²²⁸ The MOFs synthesized via
715 iono-thermal synthesis are usually negatively charged structures, So, the cations of the ILs persist
716 inside the structure as counterions to allow the structure to have electrical neutrality. The first
717 report on the synthesis of MOF-IL composites was published in 2004 where [Bmim][BF₄] IL was
718 used as a solvent for the successful synthesis of MOF-IL composite. After that many researchers

719 have reported the synthesis of MOF-IL composite by iono-thermal technique.²²⁹ Huang et al.²³⁰
720 effectively synthesized IL-MOF composite by incorporating [C_nmim][BF₄] (n=4, 6, 8, 10) IL into
721 the nanostructure of ZIF-8 MOF. Ban et al.²³¹ combined MOF-IL composite via iono-thermal
722 route of ZIF-8 with [Bmim][NTf₂] and later dispersed them in a PSf membrane to form the
723 composite membrane. The composite membranes based on ZIF-8-[BMIM][NTf₂] were compared
724 with the other membranes with polymer-IL blending and pure IL-ZIF-8-based membranes. The
725 results of gas permeation showed negative effects on the permeabilities of all the gases which
726 ultimately results in their high selectivity compared with the other membranes.²³¹ The iono-
727 thermal strategy for MOF-IL synthesis is quite an easy, and environmentally friendly way. The
728 strong interaction between the MOFs and cations of ILs exhibited some different properties of
729 MOF-ILs composite than the original IL. However, there are still some categories of ILs exist that
730 can replace the organic solvents/water as a reaction agent and there are some MOFs available that
731 cannot be charged. That is why the kinds of MOFs and ILs that can be utilized for the iono-
732 thermal synthesis are very limited, which can restrict the wider utilization of this strategy for
733 MOF-IL composite.⁴⁶ The other major drawback of this method is that the cations of ILs were not
734 able to perform the same as they were likely to perform in their bulk form. However, the
735 previously reported studies of combining MOFs and ILs through iono-thermal synthesis are not
736 popular. From the above discussion, we can conclude that the synthesis of MOF-IL composites
737 through iono-thermal process is a very difficult way because organic MOF legends comprise
738 functional groups whose reactivity with w.r.t IL increases at higher temperatures.²³²

739 **4.2. Post-synthesis modifications**

740 The synthesis of MOF-IL composite via post-synthesis modification involves the introduction of
741 an IL inside the porous structure of MOFs after its successful synthesis. This method for the
742 synthesis of MOF-IL composite is considered one of the most effective ones to enhance the
743 functional properties of materials with the advantage of economic feasibility.²³³ According to the
744 strategy for post-synthetic modification of MOF-IL, the ILs can be introduced inside the pores of
745 MOFs via the following ways such as by wet-impregnation, capillary action, and the ship-in-a-
746 bottle method.^{234, 235} as shown in **Fig 11**.

747



748
 749 **Fig 11.** Ways for the synthesis of MOF-IL composite through a) wet impregnation. Reprinted from Ref.²³⁶ Copyright
 750 2020, Elsevier. (b) capillary action. Reprinted from Ref.¹⁷⁴ Copyright 2022, Elsevier (c) the ship-in-a-bottle.
 751 Reprinted from Ref.²³⁶ Copyright 2020, Elsevier.

752 4.2.1. Wet impregnation

753 In the wet impregnation method, an inert solvent is used to dissolve the ILs and then the
 754 synthesized MOFs are added to the solution of ILs with stirring for some time at room
 755 temperature. The solvent is then removed and the desired MOFs-ILs are obtained. Imidazolium-
 756 based ILs are usually used in this method to impregnate the MOFs, such as NH₂- MIL-101(Cr),
 757 MIL-101(Cr), CUBTC, MIL-101(Fe), ZIF-8. The MIL-101- IL composite material was prepared
 758 by Jhung et al.²³⁷ in which the IL [Bmim][Cl] was dipped into the highly porous MIL-101 (Cr) in
 759 the presence of dichloromethane as an inert solvent. Zeeshan et al.²³⁸ use wet impregnation to
 760 incorporate the MOF-ZIF-8 with the IL [Bmim][SCN] and investigate their performance for the
 761 separation and adsorption of different gases. The materials incorporated with ILs showed
 762 CO₂/CH₄ and CO₂/N₂ selectivity 2.6 and 4 times higher compared with the pure ZIF-8
 763 membranes. Similarly, Mohammed et al.²³⁹ combine the IL [Emim][Ac] into MOF-177 and MIL-
 764 101 via both impregnations (dry and wet). The result that [Emim][Ac]@MOF-177 synthesized via

765 wet impregnation showed good enhancement for CO₂ uptake up to 0.3 mmol/g at 0.15 bar and
766 303 K.²³⁹ The wet impregnation strategy for MOF-IL synthesis is the mostly used and easiest way
767 to operate and the composite can be synthesized at RT under mild conditions. However, the poor
768 stability of MOF-IL composite material due to physical interaction between the MOF and IL is the
769 big question mark on the wide utilization of this strategy for a wide range of MOF-IL
770 composites.²³⁶

771 **4.2.2. Capillary method**

772 In addition to the wet-impregnation method, there is also the capillary method, which eliminates
773 the need to use solvents for the synthesis of MOF-IL composite. This method for composite
774 synthesis involves the pre-heating of MOFs in vacuum conditions for the removal of impurities
775 prior to the synthesis of composites. Then the MOFs with IL are ground and mixed well to form
776 a fine powder. The composite was then heated for several hours to increase the diffusion of IL
777 into MOF.^{240, 241} Fujie et al.²⁴² synthesized MOF-IL composite incorporating IL 1-ethyl-3-
778 methylimidazolium bis (trifluoromethyl sulfonyl) amide ([Emim][NTf₂]) within the micropores of
779 ZIF-8 MOFs. The mixture of IL ([Emim][NTf₂] and ZIF-8 was then heated and stored to enhance
780 the diffusion of [Emim][NTf₂] into micropores of ZIF-8 through capillary action.²⁴² A major
781 advantage of the capillary action strategy is that it can be used for a wide variety of ILs and MOFs
782 through direct mixing without involving any solvent. The disadvantages of this technique are
783 improper outcomes due to degradation and contamination of MOFs and ILs. One of the other
784 disadvantages is that it takes a longer time involving high temperatures to attain the uniform
785 dispersion of ILs into MOF pores.⁴⁶

786 **4.2.3. Ship-in-a-bottle method**

787 Ship-in-a-bottle is another strategy used for the synthesis of MOF-IL composite consists of the
788 direct synthesis of IL molecules into the pores of MOF.²³⁴ This synthesis technique for MOF-IL
789 composites involves the diffusion of small precursors of ILs (ship) into the pores of MOFs (bottle)
790 after dissolving into the solvents. There is a reaction between them within the MOF cages, which
791 leads to the formation of bulk ILs within the pores inside the MOF cages. At the end of the
792 process, the unreacted precursors of IL are removed by using a solvent from the surface of MOF,
793 and then IL-MOF composite is obtained once the drying process has been completed. Using this
794 method, ILs can be trapped in the cavities of the MOFs due to the large size of the synthesized ILs

795 compared to the pores within the MOFs.²⁴³ Using the ship-in-a-bottle technique MOFs-IL system
 796 was made consisting of [APMIM]Br-NaY host guest system in which an amine-functionalized IL,
 797 [APMIM]Br, was *in-situ* encapsulated in the super cages of NaY. They concluded that these host-
 798 guest systems showed good capture for CO₂ with an uptake capacity of up to 4.94 mmol.g⁻¹.²⁴⁴
 799 The key advantage of this technique is that it blocks the effects of leaching and instability of ILs
 800 produced during simple impregnation of MOF-IL composite which could give instability and
 801 degradation of the composite membrane to give the better thermophysical stability and gas
 802 separation of a well-developed and effective hybrid composite system.²⁵

803 From the above discussion, it can be referred that the synthesis of MOF-IL composites through
 804 ion iono-thermal way is difficult due to the thermal liability of functionalized groups containing
 805 organic legends which could result in problematic solubility of targeted molecules from the
 806 mixture components. However, instead of having the limitation of using some specific ILs and
 807 MOFs, the effective functional group attachment with host MOF molecule and synthesis method
 808 could be beneficial to get some good quality products. On the other hand, post-synthesis
 809 modification offers successful integration of IL with the MOF structures after the successful
 810 synthesis of MOFs. This strategy is most simple, straightforward, and effective due to the large
 811 variety in selection between the MOFs and ILs to provide a large combination of MOF-IL
 812 composite within less time. **Table 9.** shows the various methods used for the synthesis of MOFs-
 813 IL composite.

814 **Table 9.** Various methods used for the synthesis of MOFs-IL composite.

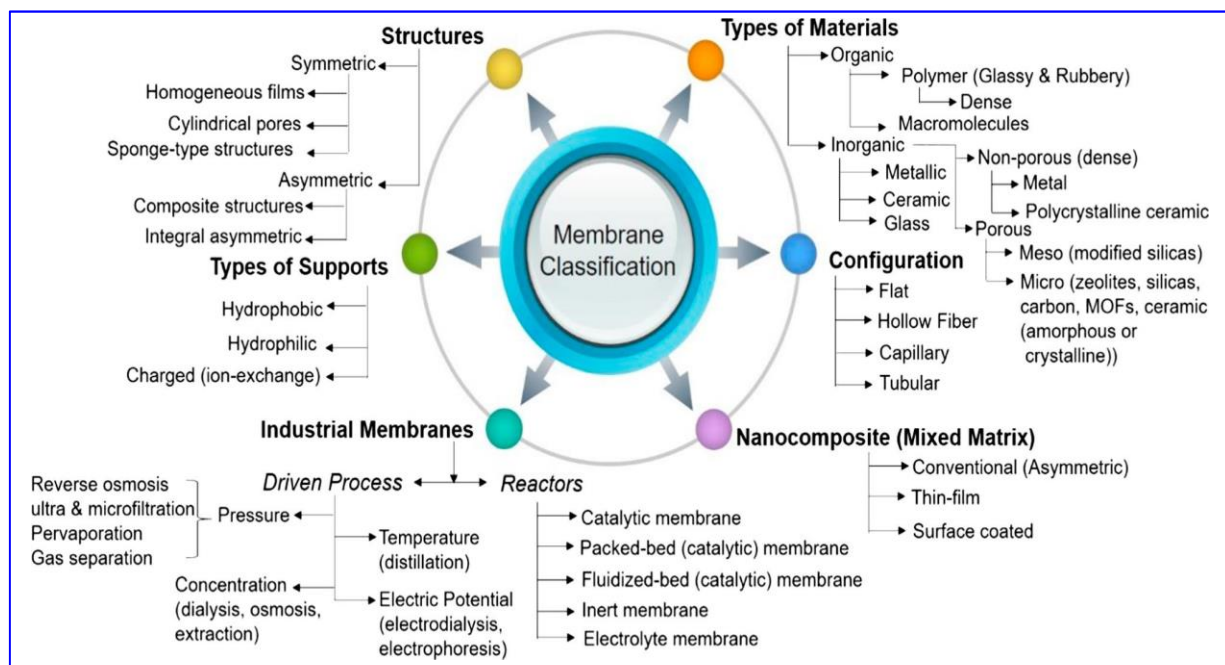
Sr No's	MOF	IL	Synthesis method	Ref
1	ZIF-8	[Bmim][NTf ₂]	Iono-thermal	
2	ZIF-8	[Emim][Br]	Iono-thermal	245
3	CuBTC	[Bmim][PF ₆]	Impregnation	246
4	CuBTC	[Bmim][BF ₄]	Impregnation	247
5	ZIF-8	[Bmim][SCN]	Impregnation	238
6	MOF-177	[Emim][Ac]	Impregnation	239
7	MIL-101	[Emim][Ac]	Impregnation	239
8	rGA	[Bmim][PF ₆]	Impregnation	248
9	MIL-101	[Bmim][Cl]	Impregnation	249
10	UiO-66	(PSMIMHSO ₄)	Impregnation	250
11	MIL-101(Cr)	EIMS-HTFSA	Capillary action	251
12	ZIF-8	EMI-TFSA	Capillary action	252
13	CuBTC	[Emim][EtSO ₄]	Capillary action	253
14	MIL-101(Cr)	(IMIZ-BAIL and TEDA-BAIL)	Ship-in-a-bottle	234

15	Na Y	[APMIM]Br	Ship-in-a-bottle	244
16	MIL-101(Cr)	[Bmim][Br]	Ship-in-a-bottle	243

815

816 5. Mixed Matrix Membranes/ (MOF-IL) Composite Membranes for CO₂ capture

817 In recent studies, Membranes based technology has received great attention towards carbon
818 capture and separation due to their advantage of high separation efficiency, low energy
819 requirement, cost-effectiveness, continuous operation, and process flexibility along with the
820 advantage of minimum carbon footprint.²⁵⁴ In particular, Mixed Matrix Membranes (MMMs)
821 have shown high capability towards gas separation by combining the properties of two different
822 materials in a single way.²⁵⁵ One of the components of MMMs is a polymeric material that forms
823 a continuous phase known as a matrix and the other one is the filler that forms a dispersed phase,
824 it may be organic or inorganic. Both the filler and matrix are immiscible with each other and
825 exhibit different transport properties.²⁵⁶ MMMs showed great potential to combine synergistically
826 the gas separation performance of porous nanostructures with polymers which can cross the
827 Robeson upper bound by limiting the trade-off in selectivity and permeability.²⁵¹ MMMs are
828 generally categorized based on geometry and nature. Due to their large range of applications, they
829 are further sub-categorized based on material type, support, configuration, structure, composition,
830 driving process, and reactions in the industry. **Fig 12.** shows the classification of membranes
831 based on different parameters and applications.



832

833 **Fig 12.** Classification of membranes based on different parameters and applications. Reprinted from Ref.²⁵⁷ Copyright
834 2017, Elsevier

835 The right choice of filler is highly inevitable in the fabrication of MMMs.²⁵⁶, otherwise, in some
836 cases, poor morphology of fillers and their interactions with the polymer matrix damages the
837 performance of MMMs.²⁵⁸ The filler should have high selectivity as a dispersed phase must
838 correspond to their size, shape, and other efficient properties that facilitate CO₂ transport.
839 Furthermore, the size of the selected filler particle should be small, and the thickness layer should
840 be several micrometers to be employed in the industrial application of membrane gas
841 separation.²⁵⁹ Different porous fillers such as silica.²⁶⁰, zeolite.²⁶¹, carbon nanotubes (CNTs).²⁶²,
842 graphene.^{263, 264}, and have been investigated for the fabrication of high-performance MMM. But
843 MOFs have especially received a great deal for various applications. because of their unique
844 structure design and tunability in comparison to other porous materials. MOFs are effective
845 adsorbents for CO₂ capture because of their large surface areas, wide range of structures,
846 composition, and porosity.²⁶⁵ Moreover, MOFs can be hybridized with metal oxides, carbon-based
847 materials, metal nanoparticles, and conducting polymers to obtain more advanced materials with
848 higher performance. Chronopoulos et al.²⁶⁶ presented a comprehensive review of hybridized
849 MOFs with CNTs to get high conductivity and stable advanced materials that can be applied in
850 numerous fields such as gas separation, storage, water purification, and energy to get some better
851 performance than unhybridized MOFs. Sosa et al.²⁶⁷ presented a review of different modification
852 strategies applied for the successful synthesis of MOF hybrids such as (covalent/non-covalent
853 modification) which have a great performance towards gas storage and separation, drug delivery,
854 and energy storage. Kalaj et al.²⁶⁸ reviewed the recent advances in the synthesis of MOF/polymer
855 composites for desalination, heavy metal, and textile dye removal applications. Alfe et al.²⁶⁹
856 reported the CO₂ storage capacities of three BTC-based MOFs with different metallic centers (Cu,
857 Al, and Fe) and graphene hybridizations and found enhanced CO₂ adsorption over CH₄ at low
858 pressure (<0.2 MPa). A review reported by Gargiulo et al.²⁷⁰ presented the successful
859 hybridization of MOFs with ILs for enhanced chemical sensing application. The hybridization of
860 high surface area and porous MOFs with tunable nature IL with possible functionalization has a
861 great future towards improving their thermochemical properties.

862 In recent years, the fabrication of composite membranes through the integration of MOFs with ILs
863 has received great attention in enhancing the gas separation performance of membranes. The

864 tunable nature of ILs, along with the advantage of high thermal stability, nonvolatility,
 865 recyclability, and inflammable nature²⁷¹ made them an efficient candidate to be used as a
 866 promotor with MOFs to enhance the gas separation of composite membranes.²⁷² MOFs-IL
 867 composite membranes can be synthesized based on a similar procedure discussed above for the
 868 synthesis of MOFs-IL composites. Chen et al.²⁷³ synthesized MOF-IL composite membranes via
 869 wet impregnation integration IL [Bmim][NTf₂] with MOF-801 and PIM-1 and resulted that the
 870 addition of MOF-IL with PIM-1 successfully enhances the CO₂ permeability and CO₂/N₂
 871 selectivity of about 5880 ± 272 and 23.9 ± 1.2 compared with PIM-1 membranes with
 872 permeability and selectivity of about 4110 ± 143 and 20 ± 0.8 respectively. Moreover, the addition
 873 of MOF-IL also enhances the anti-aging, anti-plasticization, and long-term stability of composite
 874 membranes.²⁷³ Li et al.²⁷⁴ also used wet impregnation to synthesize composite membranes
 875 combining the IL [Bmim] [NTf₂] with ZIF-8 and then integrating them with Pebax. The results of
 876 gas permeation revealed that the addition of MOF-IL with the Pebax enhances the CO₂
 877 permeability and CO₂/N₂ selectivity by 45% and 92% respectively compared with Pebax
 878 membranes. Moreover, the tensile strength and break elongation also improved by 20% and 280%
 879 respectively.²⁷⁴ **Table 10.** compares the advantages and disadvantages of MOF-IL composite
 880 membranes over MOF-based composite membranes and SILMs. In one of our studies, we
 881 synthesized Cu_xMg_x MOF via hydrosolvo-thermal reaction, integrated them with humidified IL
 882 [P₆₆₆₁₄] [Cl], and then deposited them of PTFE support to fabricate a composite membrane. Single
 883 gas permeation tests were performed for the CO₂/N₂ mixture. The results of gas permeation state
 884 that the addition of MOF-IL solution successfully enhances the CO₂ permeability and CO₂/N₂
 885 selectivity by 2937 barrer and 33.2 respectively. Moreover, the composite membrane also showed
 886 good stability under the water loadings of 30 wt.% and 50 wt.%.²⁷²

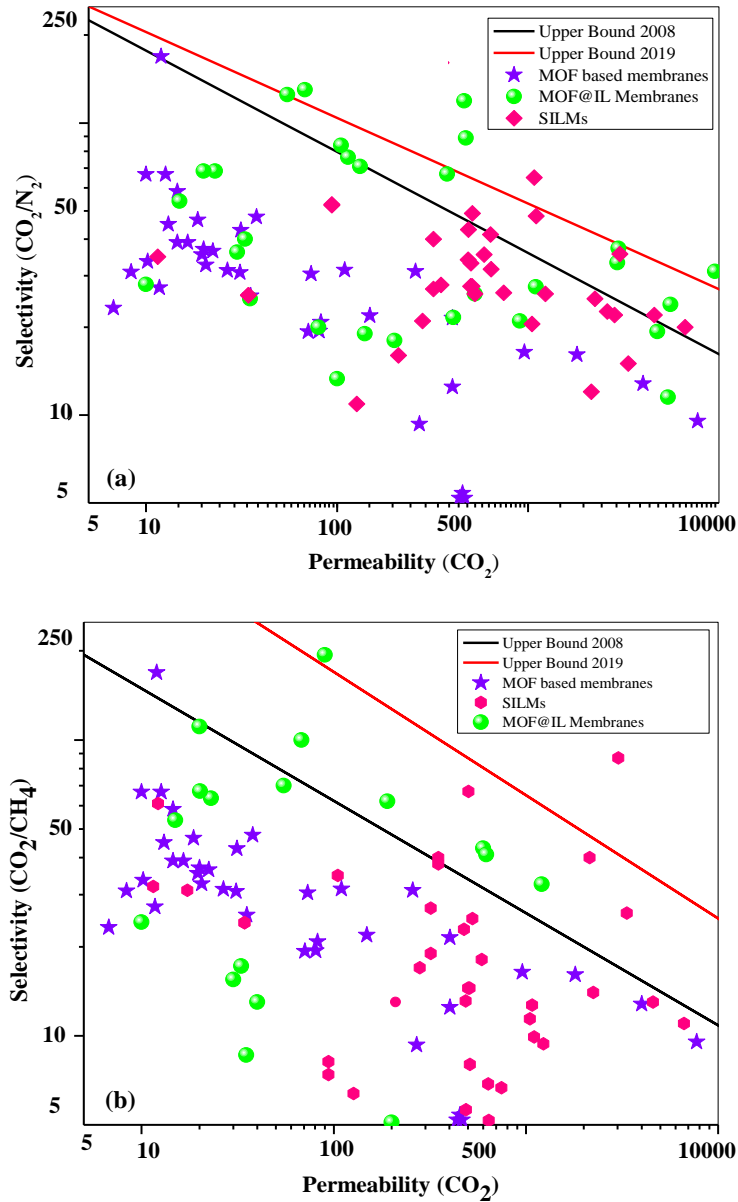
887 **Table 10.** Comparison of advantages and disadvantages of MOF-IL composite membranes over pure MOF and
 888 SILMs. Reprinted from Ref.¹⁷⁴ Copyright 2022, Elsevier

MOF based membranes	SILMs	MOF-IL composite membranes
Advantages	Advantages	Advantages
Great pore structure to distribute gas through itself	Enhance membrane selectivity compared to IL itself	Overcome permeability-selectivity trade-off limit
high surface area for CO ₂ adsorption	Poor solvent retention	Improve MOF structure on the membrane by adding IL as a supporter
Provide better adsorption performance with higher valences metal	RTIL with polymerizable groups may be converted into solid, resulting in dense composite membranes and a friendly procedure Simultaneous extraction and stripping on	Improve the separation performance because the CO ₂ adsorption capacity increase

	both sides of the ILM lower the recycling energy needs and synthesis cost	
Disadvantages	Disadvantages	Disadvantages
High operation temperature can add disturbances to the MOF crystal structure stability	High viscosity	The need to find suitable IL and MOF pairs to obtain good structural stability
Highly hydrophilic and easily binds the surrounding moisture into its pores	Transmembrane pressure owing to the IL leaching process	Does not always provide the highest permeability compared to IL or MOF alone
Difficult to regenerate the MOF	The mechanical strength of the composite degrades as the IL concentration increases	

889

890 Nasir et al.²⁷⁵ investigated the CO₂/CH₄ performance of composite membranes integrated with
891 EDA and HA-modified SAPO-34 and PES matrix and incorporated them with IL [Emim][NTF₂].
892 They resulted that the incorporation of a modified PES matrix successfully enhances the CO₂/CH₄
893 separation performance of composite membrane ~37 folds higher compared with pure PES
894 membrane. Rajati et al.²⁷⁶ synthesized NH₂-MIL-101(Cr) MOF and then impregnated them with
895 IL [Bmim][NTf₂] to fabricate a composite membrane. They resulted that 7 wt.% of MOF-IL
896 loadings successfully improved the CO₂ permeability and CO₂/CH₄ selectivity to 162% and 224%
897 respectively compared with pure Matrimid membranes. Moreover, synthesized composited
898 membranes also enhance the tensile strength and young's modulus of Matrimid membranes by
899 25% and 37% respectively. Based on the several studies reported above, here is some data
900 available in **Table 11** and **Table 12** that combines and compares the CO₂/N₂ and CO₂/CH₄
901 separation performance of MOF-IL composite membranes with the Robeson's 2008 and 2019
902 upper bound correlation of CO₂/N₂ and CO₂/CH₄ mixture with both MOFs and SILMs as shown
903 in **Fig 13a-b**. From the figure it can be stated that MOF-IL composite performs well in CO₂
904 permeability and selectivity for both post-combustion (CO₂/N₂) and pre-combustion (CO₂/CH₄)
905 than MOF and SILMs to cross the crosses the Robeson's upper bound curver 2008 and 2019 to
906 give ever better CO₂ separation from the both (CO₂/CH₄) and (CO₂/CH₄) gas mixtures.



907

908 **Fig 13.** Robeson's upper bound comparison of permeability and selectivity of MOF-IL membranes in **Table 10-11**
 909 with MOF-based membranes and SILMs a) CO₂/N₂^{277,278} b) CO₂/CH₄^{279,257,280}

910 **Table 11.** CO₂ Permeability and (CO₂/N₂) selectivity of different MOFs-IL composite membranes at different
 911 pressure and temperature.

MOF/IL Composite membrane	Driving Conditions (Pressure, Temperature)	Permeability (PCO ₂) (Barrer)	Selectivity (CO ₂ /N ₂) (a)	Ref
MOF-801@[Bmim][NTf ₂]-PIM (1%)	4 bar, 35°C	5580	23.9	273
ZIF-8@[Bmim][NTf ₂]-PSF	6 bar, 30°C	463	119	281
		473	88.9	
		377	66.8	

GO@IL-NH2-Pebax	4 bar, 25°C	114.4±5.3	76.3±3.9	263
UIO-66-(OH)2@PIL-Pebax	--	132	71	282
[Bmim][NTf2] @ZIF-8/Pebax 1657	1 bar, 25°C	104.9	83.9	274
[Emim][B(CN)4]/ZIF-8/P[vbim][NTf2]	3.5 bar, 35°C	906.4	21	283
[Emim][NTf2]/SAPO-34/P(vinyl-IL)	1-1.5 bar, 23°C	527.2	26	284
Cu _x Mg _x MOF@[P ₆₆₆₁₄] [Cl]-PTFE	2 bar, 25°C	2937	33.26	272
ZIF-8@IL-CS membrane	2 bar, 50°C	5413 ± 191	11.5	285
HKUST-1 /IL-CS membranes		4754 ± 1388	19.3	
SBS-g-POEM@IL membrane	---	407	21.6	286
ZIF-67@[NH2-Pmim] [NTf2]	---	9536	31	287
NH ₂ -MIL-101(Cr)@[C ₃ NH ₂ bim] [NTf2]-PIM	3 bar, 25°C	2979	37.24	288
HKUST-1@[emim][NTf2]-6FDA-durene	2.02 bar	1100	27.50	289
[EMIM][OTf]@Cu ₃ -(BTC) ₂ @Matrimid membrane	0.7 bar, 30°C	68	130	290
[EMIM][BF ₄]@Cu ₃ -(BTC) ₂ @Matrimid membrane		55	125	
[APTMS][Ac] & PZI20; PSF		15 ± 0.75	54.00 ± 0.95	
[APTMS][Ac] & PZ30; PSF	10 bar, 25°C	23 ± 0.94	68.49 ± 0.68	291
[APTMS][Ac] & PZI30; PSF		20 ± 0.91	68.50 ± 1.20	
[Bmim][BF ₄]/MIL-53(Al)		4-35	9-24.2	
[Bmim][PF ₆]/MIL-53(Al)	(1-5 bar),	5-33	14-39.5	292
[Bmim][CF ₃ SO ₃]/MIL-53(Al)	25°C	2-30	14.5-36.1	
[Bmim][BF ₄]/CuBTC (5wt%)		200	18	
[Bmim][BF ₄]/CuBTC (20 wt%)	(0.1 & 50 bar),	140	19	247
[Bmim][BF ₄]/CuBTC (30 wt%)	25°C	80	20	
[Bmim][BF ₄] ZIF-8	0.5 bar, 25°C	100	13.3	241
[Bmim][PF ₆] ZIF-8	0.5 bar, 25°C	10	28	293

Table 12. CO₂ Permeability and (CO₂/CH₄) selectivity of different MOFs-IL composite membranes at different pressure and temperature.

Composite membrane	Driving Conditions (Pressure, Temperature)	Permeability (PCO ₂) (Barrer)	Selectivity (CO ₂ /CH ₄) (α)	Ref
[EMIM][OTf]@Cu ₃ -(BTC) ₂ @Matrimid membrane	0.7 bar, 30°C	68	100	290
[EMIM][BF ₄]@Cu ₃ -(BTC) ₂ @Matrimid membrane		55	70	
[APTMS][Ac] & PZI20; PSF		15 ± 0.75	53.57 ± 1.07	
[APTMS][Ac] & PZ30; PSF	10 bar, 25°C	23 ± 0.94	63.51 ± 0.95	291
[APTMS][Ac] & PZI30; PSF		20.12 ± 0.91	67.07 ± 1.17	
SAPO-34[Emim][NTf ₂]; PES	10 bar, 29°C	600	43	294
Copper zinc bimetallic imidazolate (CuZnIF); PEBA	10 bar, 27°C	190	62	295
[Bmim][BF ₄]/MIL-53(Al)		4-35	3.3-8.6	
[Bmim][PF ₆]/MIL-53(Al)	(1-5 bar),	5-33	4.7-17.2	292
[Bmim][CF ₃ SO ₃]/MIL-53(Al)	25°C	2-30	4.7-15.5	

[Bmim][BF ₄]/CuBTC (5 wt%)		200	5.1	
[Bmim][BF ₄]/CuBTC (20 wt%)	(0.1 & 50 bar),	140	4.3	247
[Bmim][BF ₄]/CuBTC (30 wt%)	25°C	80	3.8	
VZIF-67/6FDA-Durene	2 bar, 35°C	1210	32.5	296
[HEMIM][N(CN) ₂] ZIF-8	1 bar, 25°C	20	111	297
[Bmim][NTF ₂] ZIF-8	1 bar, 25°C	621	41	281
[Bmim][BF ₄] ZIF-8	1 bar, 25°C	90	194	298
[Bmim][BF ₄] ZIF-8	0.5 bar, 25°C	100	4	241
[Bmim][NTF ₂] NH ₂ -MIL-101 (Cr)	10 bar, 35°C	19.2	113.1	276
[Bmim][PF ₆] ZIF-8	0.5 bar, 25°C	10	24.2	293
[Bmim][MeSO ₄] MIL-53(Al)	(0.01-5 bar), 25°C	5-40	13-4	299
[TSIL (TMGHIM)] ZIF-67	1 bar, 25°C	15.4	2.6	300

912

913 6. Techno-Economic analysis of MOFs and ILs to Capture CO₂

914 The economic cost of applying MOFs for CO₂ capture is associated with the material and
915 production cost of MOFs, its process cost, recycling/regeneration, and adsorption/desorption cost
916 of MOFs. Besides that, the cost of producing MOFs is still very high due to the costliness and
917 inaccessibility of raw materials. However, producing MOFs for industrial purposes is still
918 challenging, hindering their high-scale commercialization for industrial gas separation. **Table 13.**
919 compares the strengths and weaknesses of different materials and solvents. Normally, it is stated
920 that MOFs possess a high working capacity to capture CO₂ than their comparative carbon capture
921 materials. But their high recycling cost, upside potential, humidity effect, selectivity, and low
922 stability at high temperatures are such characteristics that need to be optimized for their higher
923 commercialization. Alkanolamines are the mostly reported solvents for post-combustion industrial
924 gas separation, producing degradation of the adsorption column. But the high heat capacity of
925 alkanol amines brings about a high regeneration cost. Thus, replacing alkanol-amines with MOFs
926 is the most feasible approach which does not consume too much energy during regeneration but
927 also reduces the process cost. DeSentis et al.³⁰¹ did a techno-economic analysis to get into
928 reducing the production cost of different MOFs-based adsorbents (HKUST, Ni-MOF, MOF-5,
929 and Mg-MOF-74). They found that the cost of solvent synthesis is a key factor to adds to the
930 higher the cost of overall synthesis cost. However, by shifting the process from solvothermal to
931 liquid-assisted grinding and aqueous synthesis the synthesis cost reduces to 13-\$36/kg from the
932 35–75\$/kg of the base cost. On the other side, ILs offer magical properties to capture CO₂.
933 However the commercialization of ILs for CO₂ capture requires further investigation into the
934 transport properties and process design parameters. However, it should be realized that the

935 research on ILs-based CO₂ separation is a relatively new and emerging area, that faces the issues
 936 of the higher cost of ILs synthesis to fulfill the higher demand on an industrial scale. Therefore,
 937 the researchers in this area are trying hard to make the ILs low-cost to make their
 938 commercialization for the industrial revolution. One of the recent modeling and simulation studies
 939 by Chen et al.³⁰² refers to the production of ILs at a low cost (\$1.24 kg⁻¹), which is quite comparable
 940 in comparison with the cost of organic solvents such as ethyl acetate or acetone cost (\$1.30–\$1.40
 941 kg⁻¹). A study by Rive et al.³⁰³ proposed an operating cost of 83 USD/t CO₂ using [Emim] [NTf₂]-
 942 IL for post-combustion CO₂ capture. Similarly, another simulation study using ASPEN referred to the
 943 extraction of aromatic hydrocarbons from an aliphatic hydrocarbon with a possible profit margin of
 944 €20 million per year.³⁰⁴ These outcomes referred that ILs are not inevitably expensive and can be
 945 fit into industrial reality if some industries become ready to take projects to invest. No doubt MOF
 946 synthesis is more expensive, time-tracking, and complicated than ILs, but their integration could
 947 be a great benefit to reducing production costs. MOFs provide extra support to ILs which can
 948 prevent the leakage of ILs. Moreover, ILs provides some extra ionic transport pathway inside the
 949 pores of MOFs to improve the conductivity or separation. Finally, the integration of MOFs with
 950 ILs reduces the addition of ILs to get the optimized performance which could lower the
 951 production cost.

952 **Table 13.** Comparison of the strengths and weaknesses of different materials and solvents. Reprinted from Ref.³⁰⁵
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Material/Solvent	Selectivity	Stability	Humidity effect	Material Cost	Process Cost	Recycling Cost	Working capacity	Upside potential
MOF	Low	Low	High	Medium/High	Medium	High	High	High
Liquids amines	High	Low	Low	Low	Low	High	Medium	Low
Zeolites	Low	High	High	Low	Low	High	Medium	Low
Soda-lime	High	High	Low	Low	Medium	Very High	Medium	Low
Ionic Liquid	High	High	Low	Low	Low	Medium/High	Low	Medium

954

955 Conclusion and future direction

956 • Climate change is making life on Earth more difficult with problems, majorly as rising
 957 temperatures, and sea levels. CO₂ emission from fossil fuel power plants is one of the main
 958 contributors to climate change. The current review focuses on the application of MOFs and
 959 ILs and their hybridization for CO₂ capture. MOFs have porous coordinate nanostructures
 960 with tunable properties through functionalization strategies, making them a promising

961 candidate in carbon capture and storage (CCS). The researchers are focusing on the thermal
962 stability and capturing performance of MOFs for industrial gas separation applications. One of
963 the major bottlenecks is a need for more knowledge regarding the stability and performance of
964 MOFs under single and mixture of gases, so it is tough to get know into the actual CO₂
965 separation efficiency with possible process limitations. Moreover, the investigation of MOF
966 behavior in actual industrial conditions such as high temperatures, humid environments, and
967 high mechanical stress conditions still needs to be investigated to make their
968 commercialization feasible for industrial gas situations. Although several computational
969 approaches to gas mixtures are made, the experimental investigation is more reliable.

970 • ILs, the future solvents, are now leaving the laboratories and entering the commercial
971 industry. The tunable properties of ILs by careful selection of cation and anion make them an
972 ideal choice for CO₂ capture. Although researchers have developed ILs that are highly
973 selective to CO₂, the major issues preventing the commercialization of ILs are the high
974 viscosity, toxicity, cost, thermal stability, and purity of these solvents.

975 • To overcome the shortcomings of ILs and MOFs, researchers are focused on combining
976 MOFs and ILs to combine the exceptional properties of ILs along with the high specific area
977 of MOFs. Moreover, researchers have moved one step ahead and combined MOF-IL
978 composite with membranes to overcome the problems of ILs and MOFs when utilized
979 individually on the membrane surface. The proper amalgamation of MOFs-IL composite with
980 the membrane is required to get better dispersion to give better adhesion between the solution
981 and composite membranes to remove the unnecessary voids to provide better performance for
982 CO₂ separation. Moreover, the high viscosity of IL is also a big problem during amalgamation,
983 and low-purity and high-viscosity ILs are not selected for such applications.

984 Based on the current review, the following recommendations are suggested:

- 985 i. The stability and performance of MOFs under actual conditions need to be
986 investigated.
- 987 ii. The cost of the ILs needs to be reduced by synthesizing ILs from biobased
988 components, which would reduce the price as well as it would reduce the toxicity.
- 989 iii. The viscosity of ILs needs to be reduced by synthesizing protic ILs, which would
990 reduce the viscosity and reduce the steps required in the purification of ILs. Moreover,

991 ILs viscosity can be reduced by synthesizing ILs from ether functionalized group on
992 the cation.

993 Based on the above recommendations, it is suggested that further investigation on MOF-IL
994 composite is required to make their commercialization straightforward for industrial-based gas
995 separation applications.

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1104 **Nomenclature**

Abbreviation	Full Name
Al	Aluminum
[Ala] ⁻	Alaninate
[APMIM] [Br]	1-aminopropyl-3-methylimidazolium bromide
[APTMS] [Ac]	3-(trimethoxysilyl) propan-1-aminium acetate
[Arg] ⁻	Arginate
BDC	1,4-benzendicarboxylic acid
[B4MePyr]	1-butyl-4-methylpyridinium bromide
[BF ₄] ⁻	Tetrafluoroborate
[Bmim] ⁺	1-butyl-3-methylimidazolium
[Bmim] [BF ₄]	1-butyl-3-methylimidazolium tetrafluoroborate
[BMIM] [Br]	1-butyl-3-methylimidazolium bromide
[Bmim] [Cl]	1-butyl-3-methylimidazolium trifluoromethanesulfonate
[Bmim] [N(CN) ₂]/[DCA]	1-butyl-3-methylimidazolium dicyanamide
[Bmim] [OTf]	1-butyl-3-methylimidazolium trifluoromethanesulfonate
[Bmim] [PF ₆]	1-butyl-3-methylimidazolium hexafluorophosphate
[Bmim] [SCN]	1-butyl-3-methylimidazolium thiocyanate
[Bmim] [TCM]	1-butyl-3-methylimidazolium tricyanomethanide
[Bmim] [NTf ₂]/ [Tf ₂ N]	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide
[Bmpy] ⁺	1-butyl-3-methylpyridinium
Bpdc	4,4'-biphenyl dicarboxylate
[Br] ⁻	Bromide
CCS	Carbon capture and utilization
CH ₄	Methane
[Cho] [Gly]	Choline glycinate
[Cho] [Lys]	Choline lysinate
[Cho] [Pro]	Choline proline
[Cho] [Ser]	Choline serinate
[Cho] [Val]	Choline valinate
[Cl] ⁻	Chloride
CNTs	Carbon nanotubes
[Hmim] [NTf ₂]	1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[C ₈ H ₄ F ₁₃ mim] [NTf ₂]/[Tf ₂ N]	1-(3,3,4,4,5,6,6,7,7,8,8,8-tridecafluorooctyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

CO	Carbon monoxide
CO₂	Carbon dioxide
COF	Covalent organic framework
CU	Copper
[Cu₃(btc)₂]	1,3,5-benzenetricarboxylate
DABCO	1,4-diazabicyclo[2.2.2]octane)
[N(CN)₂] / [DCA]	Dicyanamide
DEF	N, N-diethyl formamide
DESS	Deep eutectic solvents
[DETAH] [Gly]	Diethylenetriamine glycinate
[DETAH] [Lys]	Diethylenetriamine lysine
[DMAPAH] [EOAc]	Dimethylpropylenediamine ethoxyacetate
[DMEDAH] [EOAc]	N,N-dimethylethylenediammonium ethoxyacetate
DMF	N, N-dimethylformamide
DUT-4	[Al(OH)(ndc)(DMF) _{1.5} (H ₂ O) _{1.5}]
DUT-5	[Al (OH)(bpdC)(DMF) _{1.8} (H ₂ O) _{3.5}]
EDA	Ethylenediamine
[Emim] [AC]	1-ethyl-3-methylimidazolium acetate
[Emim] [Ala]	1-ethyl-3-methylimidazolium alaninate
[Emim] [Br]	1-ethyl-3-methylimidazolium bromide
[Emim] [B(CN)₄]	1-ethyl-3-methylimidazolium tetracyanoborate
[Emim] [BF₄]	1-ethyl-3-methylimidazolium tetrafluoroborate
[Emim] [N(CN)₂] / [DCA]	1-ethyl-3-methylimidazolium dicyanamide
[Emim] [N(CN)₂] / [DCA]	1-ethyl-3-methylimidazolium dicyanamide
[Emim] [EtSO₄]	1-ethyl-3-methylimidazolium ethyl sulphate
[Emim] [Gly]	1-ethyl-3-methylimidazolium glycinate
[Emim] [OTf]	1-ethyl-3-methylimidazolium trifluoro methanesulfonate
[Emim] [TCM]	1-ethyl-3-methylimidazolium tricyanomethanide
[Emim] [NTf₂] / [Tf₂N]	1-ethyl-3-methylimidazolium bis- (trifluoromethyl sulfonyl) imide
[EOMmim] [PF₆]	1-methoxyethyl-3-methylimidazolium hexafluoroborate
[EOMmim] [NTf₂] / [Tf₂N]	1-methoxyethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide
EIMS-HTFSA	(EIMS=1-(1-ethyl-3-imidazolium)propane-3-sulfonate; HTFSA=N,N-bis(trifluoromethanesulfonyl)amide)
EMI-TFSA	(1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide)
Fe	Iron
[Gln]	Glutamine
[Gly]⁻	Glycinate
HA	Hexylamine
H₂	Hydrogen
H₂O	Water
H₂S	Hydrogen sulfide
[His]⁻	Hisdinate
[Hmim]⁺	1-hexyl-3 methylimidazolium
ILs	Ionic liquids
Lys	Lysine
MEA	Methyl ethyl amine
Mg²⁺	Magnesium ion
MMMs	Mixed matrix membranes
MOFs	Metal organic frameworks
MTV	Multivariate
Ndc	2,6-naphthalene dicarboxylate

N ₂	Nitrogen
[N ₁₁₁₄] [NTf ₂] / [Tf ₂ N]	Butyltrimethylammonium bis(trifluoromethylsulfonyl)imide
[N ₆₆₆₁₄] ⁺	Trihexyltetradecylammonium
[N ₆₆₆₁₄] [Lys]	Trihexyltetradecylammonium lysine
Ni ₃ O	Nickel (III) oxide
Ni-MOF	Nickel based metal organic framework
NO _x	Nitrogen oxides
NO ₂	Nitrogen dioxide
O ₂	Oxygen
[Omim] ⁺	1-octyl-3-methylimidazolium
[Omim] [NTf ₂] / [Tf ₂ N]	1-octyl-3-methylimidazolium bis(trifluoromethyl)sulfonylamide
PES	Polyethylsulfone
PEI	Polyethyleneimine
[PF ₆] ⁻	Hexafluorophosphate
[Pmmim] ⁺	1,2-dimethyl-3-propylimidazolium
Ppm	Parts per million
[Pro] ⁻	Prolinate
[P ₆₆₆₁₄] ⁺	Trihexyltetradecylphosphonium
[P ₆₆₆₁₄] [Lys]	Trihexyltetradecylphosphonium lysine
[PSmim][HSO ₄]	1-methylimidazolium-3-propylsulfonate hydrosulfate
QSPR	Quantitative structures property relationship
SALI	Solvent-aided ligand inclusion
[SCN] ⁻	Thiocyanate
Sox	Sulfur oxides
SO ₂	Sulfur dioxide
SO ₃ H	Sulfonic acid
[TfO] ⁻	Trifluoromethanesulfonate
[Tyr] ⁻	Trysinate
[Val] ⁻	Valinate
WGS	Water gas shift
ZIF	Zinc imidazole framework
Zn ₄ O	1,4-benzodicycarboxylic acid

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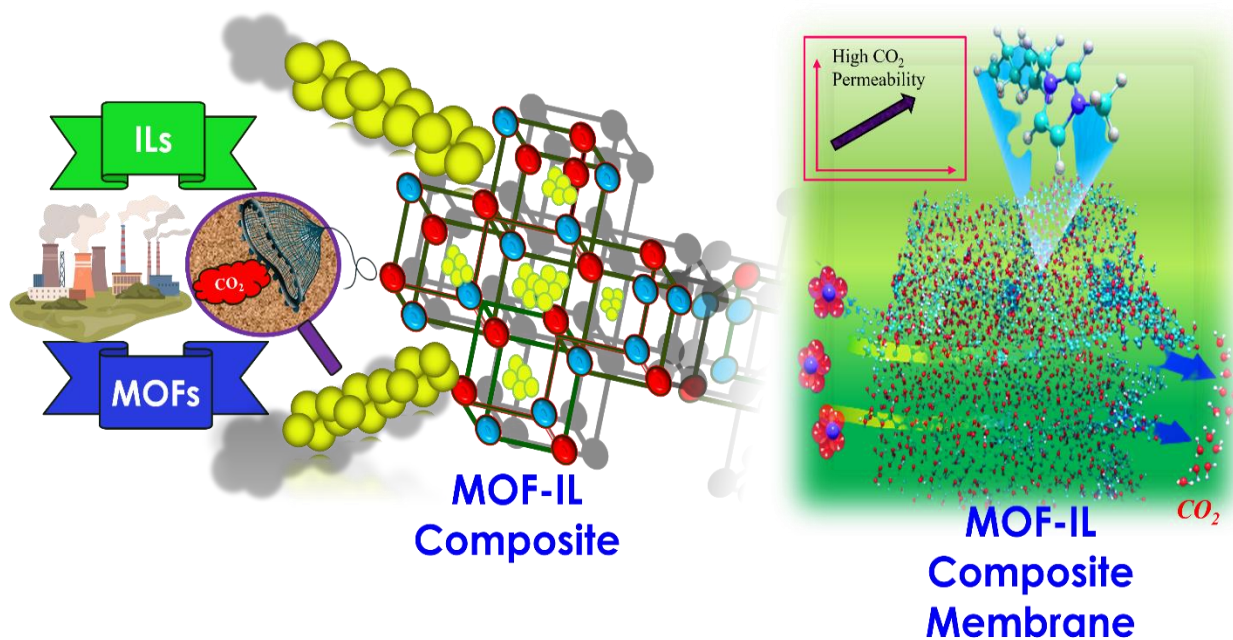
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