1 **Electronic Supporting Information (ESI)**

2 **Validation of 'lock-and-key' mechanism of metal-organic framework in**
3 **selective sensing of triethylamine**

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1. Methods and materials

1.1 Chemicals and synthesis of Al-MOF

Aluminium chloride hexahydrate ($AlCl_3.6H_2O$), 2-aminoterephthalic acid (BDC-NH_2), N,N′-Dimethyl formamide (DMF), and triethylamine (TEA) with high purity (>98%) were purchased from Sigma Aldrich. All other chemicals such as ethylamine (EA), diethylamine (DEA), toluene (T), ammonia (NH_3), pyridine (Py), formaldehyde (FA), ethyl benzene (EB), acetone (Ac), and acetaldehyde (AcA) were purchased from commercial suppliers with high purity and directly used for the analysis without any further purification.

Briefly 1.1 g of BDC-NH_2 was added into 240 mL of DMF in a 250 mL of Erlenmeyer flask. With the help of rubber stand, flask was held into the 1 L beaker containing 500 mL of water. The whole content was placed on the hot plate aided with the magnetic stirrer and the temperature was gradually raised to ~100 °C. Once temperature reached, the BDC-NH_2 was allowed to dissolve into the DMF at 550 rpm. After this, 2.996 g of $AlCl_3.6H_2O$ was slowly added within 2-3 minutes. Once all weighed $AlCl_3.6H_2O$ was added, the content was stirred at ~110 °C for 3 h. After stirring, the content was kept in a conventional oven for 18 h. The resulting content was cooled down and centrifuged to obtain yellow solid. The final solid precipitates were washed (100 mL of DMF × 3 times), filtered (0.45 μm Whatmann filter paper), and immersed in ethanol for solvent exchange (50 mL × 2 days). Finally, Al-MOF was dried at 200 °C for 12 h using conventional oven and the resulting MOF was stored in 20 mL amber bottles at ambient conditions.

1.2. Instruments for characterization

Crystalline property of the synthesized Al-MOF was investigated using D-8 Discover powder X-ray diffractometer (PXRD) (Bruker, Billercia, Massachusetts). The crystal data were collected with the angular 2θ range, scan speed, and step size of 2-20°, 0.1, and 1 sec step^{-1}, respectively. FTIR with attenuated total reflectance (ATR) mode was performed using Perkin Elmer FTIR-100 spectrometer (Akron, Ohio, USA). Raman spectrum of the MOF was acquired using BRUKER RFS 27- Stand-alone FT-Raman spectrometer (Billercia, Massachusetts, USA). The morphology was characterized using a Quanta 400 SEM (FEI, Hillsboro, Oregon). Surface area, pore volume, and pore size was analysed using Micrometrics ASAP 2010 (Norcross, USA) at liquid nitrogen temperature. Before N_2 adsorption-desorption measurement, the sample was degassed at 150 °C for 3 h. TGA

analysis was carried out using SDT Q600 with temperature ranging from 40-800 ºC in the presence of nitrogen atmosphere. The fluorescent measurement was carried out using Molecular Devices-Spectra Max M3 (Sunnyvale, California, USA).

1.3. Preparation of standards and probe solution

20 mM of working standard (WS) of TEA was prepared by mixing 3 mL of 98% TEA in 1 L of deionised water (DIW) using amber standard flask. The content was then stored in the refrigerator at 4 °C. For all experiments the sequential dilution of TEA was made from the high concentration of WS. Before the preparation of probe solution, the MOF was activated at 200 °C for 3 h. Then 0.5 g of Al-MOF was dissolved in 500 mL (probe concentration: 1 g L^{-1}) of DIW and the content was ultrasonicated for 5 minutes at the amplitude of 50%. The resulted content was stored at 4 °C and before every use the probe was sonicated in a similar manner.

1.4. Day-to-day stability of Al-MOF

Stability is an important phenomenon which restricts the practical application of MOFs in real filed. In order to improve the aqueous, thermal, and mechanical stability of the MOFs various pre- and post-synthetic approaches was performed. For instance, among those methods, the addition of Lewis basic functional groups (e.g., $-NH_2$),[1] ester groups,[2] and water repellent functional groups (e.g., trifluoromethoxy)[3] to the ligand portion of the MOF was found to be an effective option to consider. Similarly, the open metal sites and metal clusters present in the MOF was also found to be responsible for the aqueous stability of MOF (e.g., MIL-101 and MIL-53 frameworks).[4] It can be noted that the selected MOF in this study possess both functional properties such as $-NH_2$ group as well as stable metal clusters (Al^{3+}) responsible for aqueous stability of MOF. By keeping this as a key point, water stability of proposed probe was investigated on daily basis. Prior to fluorescence measurement, each day MOF probe solution was taken from the refrigerator and allowed to reach RT. After that, 3 mL of suspension was sonicated for 5 minutes and immediately subjected to fluorescent analysis.

1.5. Effect of temperature

The sensitivity of the probe against TEA was checked across eight different temperatures (RT, 30, 35, 40, 45, 50, 55, and 60 °C). For this measurement, 2 mL of probe solution (concentration: 1 g L^{-1}) was heated at specific condition with the help of instrument and corresponding fluorescent efficiency was monitored. Similarly, the effect of fluorescence intensity with respect to Al-MOF was noticed by adding 0.49 mM of TEA (final concentration) into the probe at specific temperature. In order to visually detect the changes in fluorescence of proposed probe, TEA concentration was fixed little higher (e.g.,0.49 mM).

1.6. Selectivity of Al-MOF

In an analytical point of view, it is important to ensure the selective response of the proposed sensor against TEA in the presence of potential interferences. In this respect, the sensing behaviour of Al-MOF against a variety of low molecular weight organic contaminants (such as AcA, Ac, EB, FA, Py, NH_3, and T) was investigated in both single and mixed pollutant levels. For this measurement each time a known concentration of selected pollutants (final concentration: 0.49 mM) were added into the cuvette containing 2 mL of fresh probe solution and change in fluorescence efficiency of probe was monitored. In the mixed pollutant case, the final concentration of sum of all pollutants was kept as 0.49 mM and the experiments were conducted similar with above mentioned method.

1.7. Density functional theory (DFT) calculations

This calculation was implemented by means of the pseudopotential code SIESTA.[5] More information please refer to our previous works about MOFs for adsorption of VOCs.[6] All calculations were performed using the generalized gradient approximation (GGA-PBE) including spin polarization[7] with taking into account of van der Waals correction.[8] Full optimization of atomic positions were also carried out. During this optimization, the ion cores were described by norm-conserving non-relativistic pseudopotentials[9] with cut off radii of 1.14, 1.48, 1,47, 2.06 and 1.25 a.u. for C, N, O, Al, and H, respectively; the wave functions were expanded with a double-ζ plus polarization basis of localized orbitals for non-hydrogen

115 atoms and with a double-ζ basis for H. Optimizations of the force and total energy were
116 performed with the accuracies of 0.04 eV/Å and 1 meV, respectively.

117　　Bulk structure of Al-MOF contains more than one thousand atoms per unit cell.[10] DFT
118 calculation for these bulk structures is not possible. Therefore, a part of the unit cell that
119 reproduces all feature of local environment near Al-O centers was selected and the sensing
120 mechanism was assessed. Accordingly, the stability of atomic structure of Al-MOF was
121 verified through optimization of atomic structure model. FTIR results clearly showed that
122 there were no direct interactions between TEA and amine groups (Fig. S9). From the
123 literature survey it was found that the main mechanism of MOFs with guest molecules occurs
124 between π-orbitals of aromatic rings of ligands and functional group of the guest molecules.
125 Additionally, so far there are no theoretical calculation methods available for evaluating the
126 contribution of amine groups in fluorescent sensing.[11] Therefore, based on our previous
127 experience [6] and the results obtained from FTIR analysis the amine groups were excluded
128 from the modeling studies.[10]

129　　Adsorption enthalpies were calculated by the standard formula,

130
$$\Delta H(air) = [E_{host+mol} + (E_{host} + E_{mol})]$$

131 where E_{host} and E_{mol} is the total energies of MOF and single molecules of selected species (in
132 empty box), respectively. Note that this formula describes the adsorption of molecule from
133 the air. However, in the present experimental setup, water was used as the diluent. Therefore,
134 we have evaluated the energies of interactions of MOF with water. In this case the building of
135 the exact model was found difficult task. Thus for evaluation of the energetics of interaction
136 of molecule with water (E_{water}), the estimated enthalpy of interaction with water for each
137 group of molecules were summarised. For hydrophilic groups, the estimated energy of
138 interaction with water was about 9.6 kJ mol^{-1} (see discussions in Boukhvalov et al.[12]) it was
139 about 1.9 kJ mol^{-1} for hydrophobic group.[13] From this, the enthalpy of adsorption was
140 calculated as follows,

141
$$\Delta H(water) = \Delta H(air) - E_{water}$$

142　　These calculations were performed for the zero temperature case. By taking account of
143 temperature we have also evaluated Gibbs free energy of the system,

144
$$\Delta G = \Delta H + T\Delta S$$

145 where T is the temperature and ΔS is the change of entropy of adsorbed molecule and which

146 has been estimated by considering the standard gas→ liquid transition,

$$\Delta S = \frac{\Delta H_{vaporisation}}{T}$$

147

148 where $\Delta H_{vaporization}$ is the measured enthalpy of vaporization.

149

150 **1.8. Reusability test**

151   Initially, the prepared probe solution (1 g L^{-1}) was used to sense 0.49 mM of TEA

152 molecules. Later, the MOF was centrifuged at 7000 rpm for 5 minutes to separate the solid

153 portion using filtration. The collected MOF was washed with ethanol:water (1:1 ratio). The

154 MOF powder was centrifuged from the slurry and dried in an oven at 150 °C for 2 h. This

155 recycled MOF was dispersed in water. Later, the fluorescence efficiency of this washed MOF

156 (blank-2) was noted. Change in fluorescence intensity of this recycled probe was monitored

157 (cycle 2) after introducing TEA (0.49 mM) into the probe solution. Similarly, the process was

158 repeated for other cycles.

159

160 **2. Results and discussion**

161 **2.1. Fluorescent property of Al-MOF: Results of DFT calculation part**

162   The interaction energetics of water molecules on Al^{3+} sites was initially performed. In

163 light of this simulation, the enthalpy of adsorption for water molecules from the air was

164 calculated as -232 kJ mol^{-1}. Furthermore, the Gibbs free energy of MOF at RT was calculated

165 by taking into account of adsorption from water and the value was -157 kJ mol^{-1}. The

166 magnitude of calculated value was approximately five times larger than the value of total

167 energy of hydrogen bonds per molecule in an aqueous phase (-43.98 kJ mol^{-1}).[9, 12] Therefore,

168 formation of the Al-water bonds was much more preferable for water molecules that were

169 present in the aqueous phase. In addition, this high stability of Al-MOF was also attributed

170 by the formation of robust coordination bond between water and open metal sites of Al^{3+}.[6]

171

172 **2.2. Storability of Al-MOF**

173   Although MOFs have diverse structural superiority (e.g., specific internal and external
174   surface area, wider cages/pores) still the synthesis of this material needs longer reaction time.
175   Accordingly, it would be helpful to study the storage stability of this material under ambient
176   condition. In this regard, 100 mg of synthesized MOF was kept on the laboratory table over a
177   month and at every15 days of interval, MOF probe solution (without thermal activation) was
178   prepared and their fluorescent efficiency was tested spectrometrically. Fig.S4b-d shows the
179   result of storage stability of Al-MOF over a period of 30 days. Accordingly, there was only
180   minor enhancement in fluorescent intensity after storage of 30 days at ambient condition
181   (e.g., RFU for 0 and 30 day: 238 and 280 a.u.) (Fig. S4b). This slight increase in the
182   fluorescence intensity of MOF over a period of time was attributed to the possible hydrolysis
183   of Al^{3+} centres by water molecules (formation of stable Al-water bond). Theoretically,
184   hydrolysis of Al^{3+} centres restricts the free rotation of aromatic rings of the MOF.[14] This
185   process encourages the charge transfer between n electron of –NH_2 group and the π electron
186   of the MOF. In this way, the fluorescence intensity of the MOF was increased.

187   Likewise, the results of FTIR and PXRD analysis also confirmed the structural integrity of
188   Al-MOF in water over a period of 30 days (Fig.S4c and d). Here it is noteworthy that the
189   peak responsible for in and out phase stretching of -NH_2 was observed at 3385 and 3496 cm⁻
190   ¹, respectively. Nonetheless, the intensity of these peaks was considerably reduced in water
191   dispersed phase of Al-MOF. This decrease was not visually seen in the FTIR spectrum of
192   synthesized and stored form of Al-MOF (Fig. S4c). The reason for this reduction may be the
193   possible hydrolysis of inorganic binding units (i.e., Al^{3+}).[15] This process of hydrolysis tends
194   to diminish the connectivity between the linker units and metal ions.[16] Nonetheless, the DFT
195   calculation confirmed that the hydrolysis of Al^{3+} centres did not affect the aqueous stability
196   of the framework (Refer to DFT calculation results of this section).

197

198   **2.3. Sensitivity profiles of a month stored Al-MOF**

199   In general, the structural stability of the prepared MOF could be easily destroyed by the
200   omnipresent factors such as moisture, pressure, and temperature. In order to extend the
201   applicability of the MOF to an industrial scale one should ensure the storability profile of
202   MOF at ambient conditions. Thus, the sensing efficiency of a month stored MOF against
203   diverse concentrations of TEA was also investigated (Fig.S5). Interestingly, the MOF stored
204   over a month at ambient condition showed almost similar performance with the freshly

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205 synthesized MOF (Fig.S5a). This result indicated that the physical and chemical properties of

206 the Al-MOF were not affected by atmospheric moisture and pressure.

207   Al-MOF has a tendency to react with omnipresent molecules (e.g., water, CO_2, and FA)

208 which could affect the fluorescence property of this material.[6] These adsorbed omnipresent

209 molecules could compete with the ligand units of MOF. This process disturb the actual

210 electronic transition of MOF.[17] Therefore, this change in fluorescence behaviour of MOF as a

211 function of storage time can be verified through the fluorescence calibration analysis. In this

212 context, the linear calibration of stored MOF towards diverse concentration of TEA at three

213 different storage intervals namely 0, 15, and 30 days was also carried out (Fig.S5b). The

214 obtained slope (sensitivity) values for the storage time of 0, 15, and 30 days were 3815, 3982,

215 and 3350, respectively. This closer sensitivity value along with good R^2 value ($\geq$ 0.99)

216 confirms the fluorescence stability of the sensing probe. This result provides an impression

217 that, one can use the calibration curve of Al-MOF for a month to derive the unknown TEA

218 concentrations in the aqueous solution. Overall, the MOF was not disturbed by any of the

219 omnipresent factors to give an impression that the selected Al-MOF was highly stable in all

220 kinds of fluorescent measurement. In this respect, the proposed method was accurate as well

221 as time efficient for the sensing of TEA in aqueous solution.

222

223 **2.4. Effect of temperature on sensing behaviour of Al-MOF**

224   Temperature is an important factor which affects the sensing performance of probe

225 material. In this regard, it is essential to study the behaviour of proposed probe at various

226 temperatures. Results showed that there was no significant change in fluorescence intensity

227 with respect to increase in temperature. For instance, the RFU value of MOF at RT and 60 °C

228 was 487 and 537 a.u., respectively (Fig.S6a). Although there was no significant increase, the

229 small variation (i.e., higher) in fluorescence intensity was supported by the enhanced

230 dispersion of the probe compared to RT. When temperature increases, the dispersion ability

231 of the MOF appeared to increase because of the fast solubilisation of Al-MOF in water. In

232 other words, at higher temperature physical forces such as van der Waals and hydrogen

233 bonding tend to loosen which results the solubilisation of loosely bound particles in reaction

234 medium (e.g., water).[18] In this regard, the optical density (OD) value increased which in turn

235 slightly increased the intensity of fluorescence. Similarly, the addition of 0.49 mM of TEA

236 into the probe enhanced the RFU of MOF from 487 to 2349 a.u. at RT (Fig.S6b). Likewise,

237 gradual increase in the sensing efficiency of the probe with increase in temperature was also
238 observed. Particularly the RFU of MOF@0.49 mM at RT and 60°C was 2349 and 2467 a.u.,
239 respectively. The difference in the RFU value of MOF@0.49 mM at RT and 60°C was about
240 118 units. This result indicates that there was only slight influence on the sensing ability of
241 Al-MOF with respect to temperature. Consequently, the sensing of TEA using Al-MOF was
242 suspected to be accompanied by physical process such as non-covalent bond interactions.[19]
243 These non-covalent bond interactions might be attributed to the interaction between $-CH_3$
244 portions of the TEA to the π-orbitals of the aromatic rings of the MOF.

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276

277 **Table S1.** Summary of surface area and pore volume characteristics of Al-MOF

278

Order	Type of measurement	Value
1	BET surface area	276 m^2 g^{-1}
2	Langmuir surface area	410 m^2 g^{-1}
3	t-Plot micropore area	185 m^2 g^{-1}
4	t-Plot External surface area	90.5 m^2 g^{-1}
5	Adsorption average pore diameter (4V/A)	174 Å
6	Desorption average pore diameter (4V/A)	126 Å
7	Adsorption average pore width	65.9 Å

279
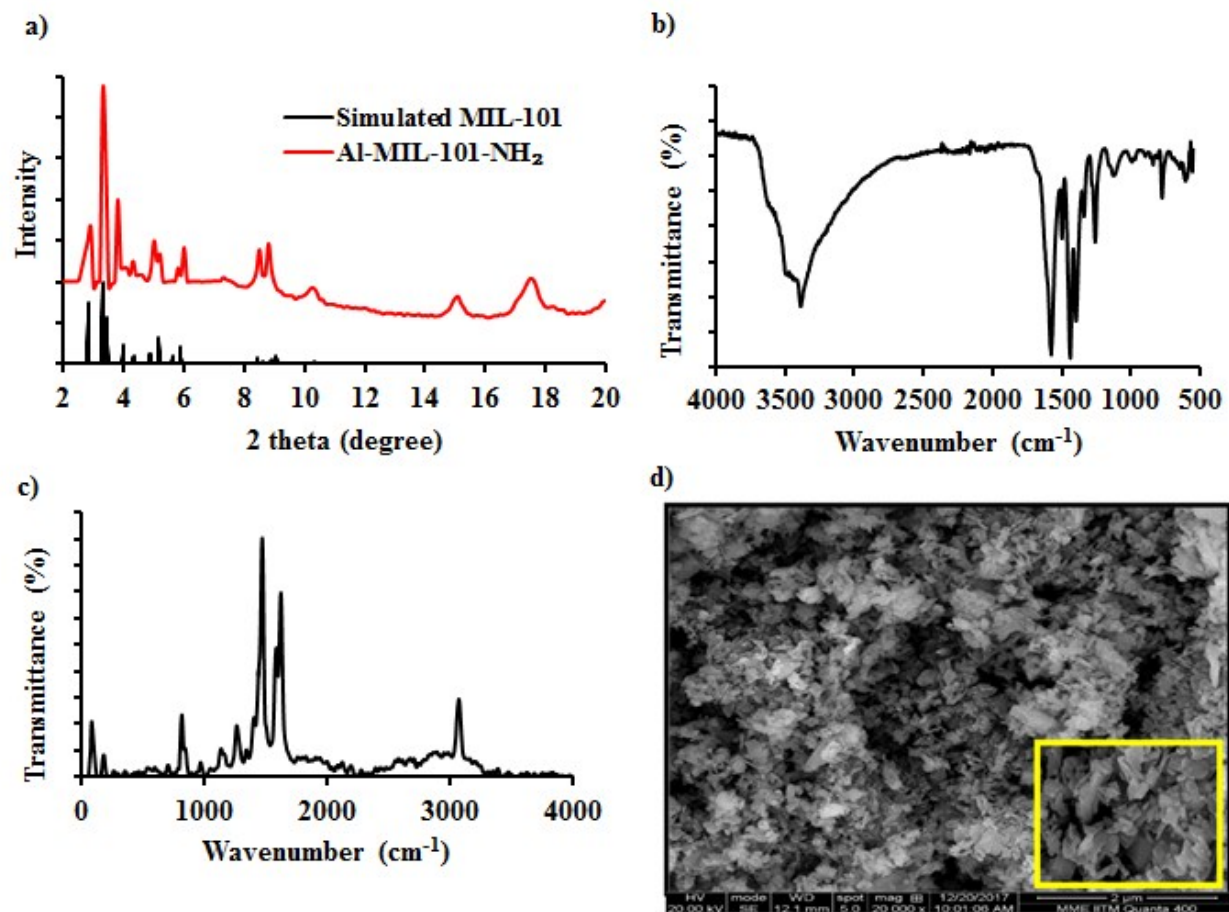
Fig. S1. Summary of a) PXRD, b) FTIR, c) Raman spectrums, and d) SEM image of synthesized Al-MOF
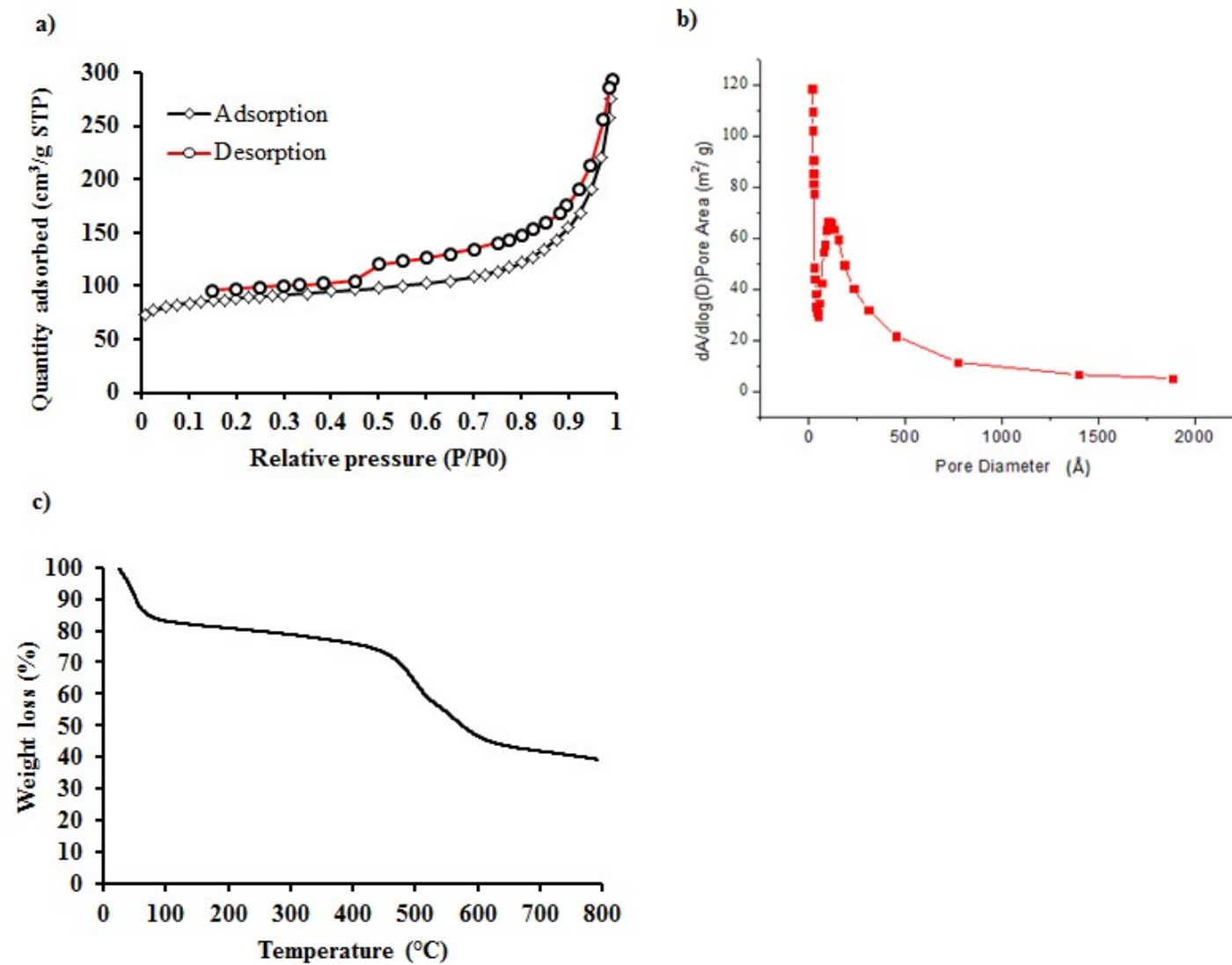
Fig. S2. N_2 adsorption-desorption isotherm (a), pore size distribution, and TGA (c) patterns of Al-MOF

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a)
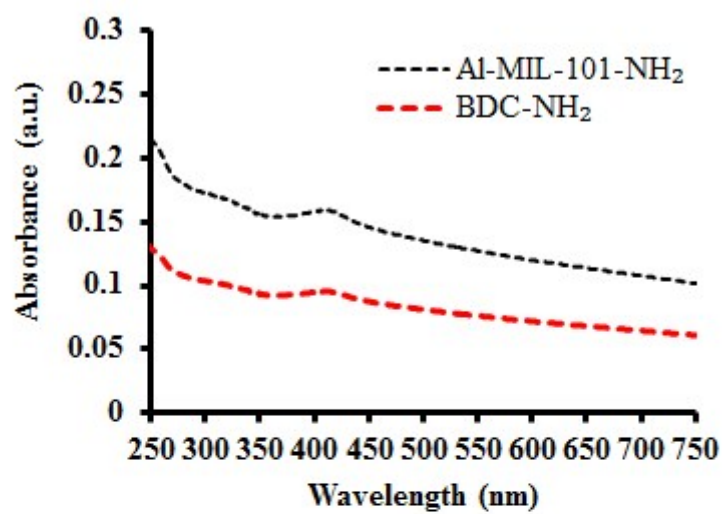
b)
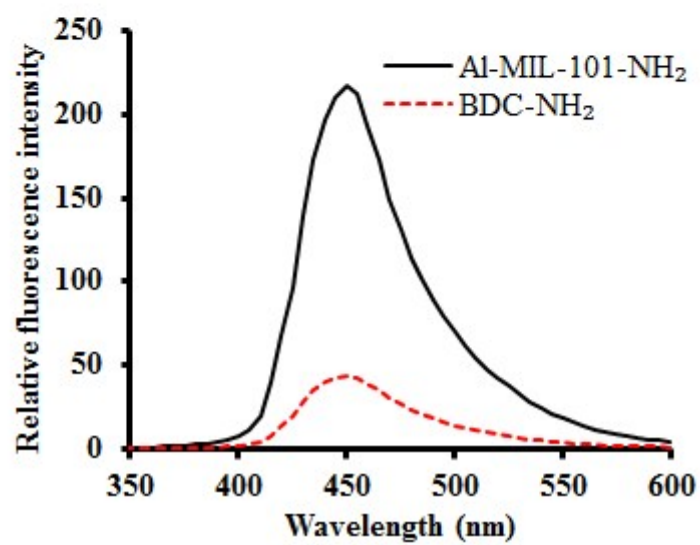
Fig. S3. Excitation and emission spectrum of ligand (BDC-NH$_2$) and MOF (Al-MOF) in aqueous phase.
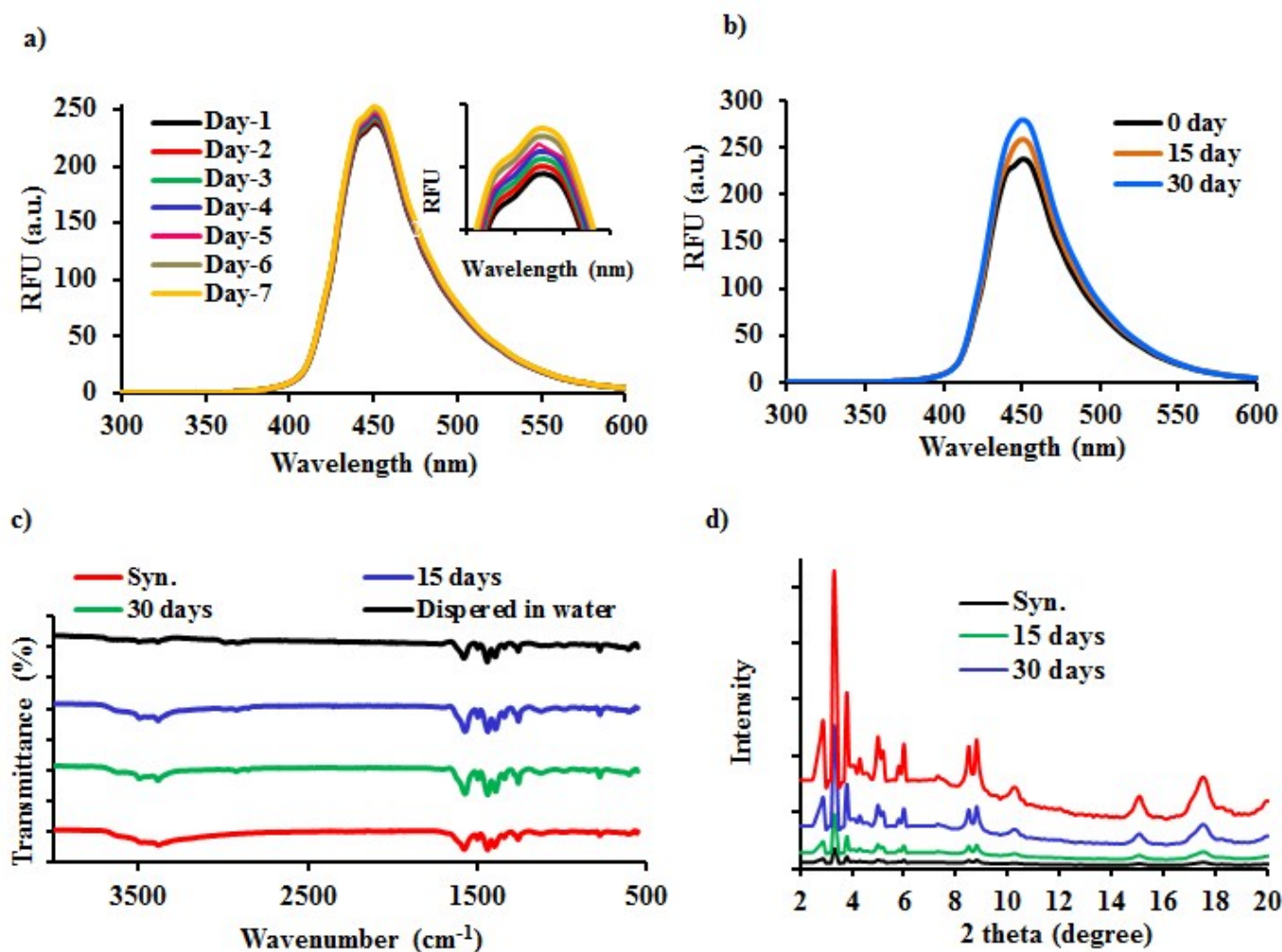
Fig. S4. Fluorescent stability of Al-MOF against diverse aqueous and ambient storage conditions. a) Day-to-day stability of Al-MIL-NH$_2$ dispersed in water b) fluorescent response of a month stored Al-MOF, c) and d) FTIR and PXRD pattern of the MOF probe solution dispersed in water and as well as stored over a month at ambient condition.
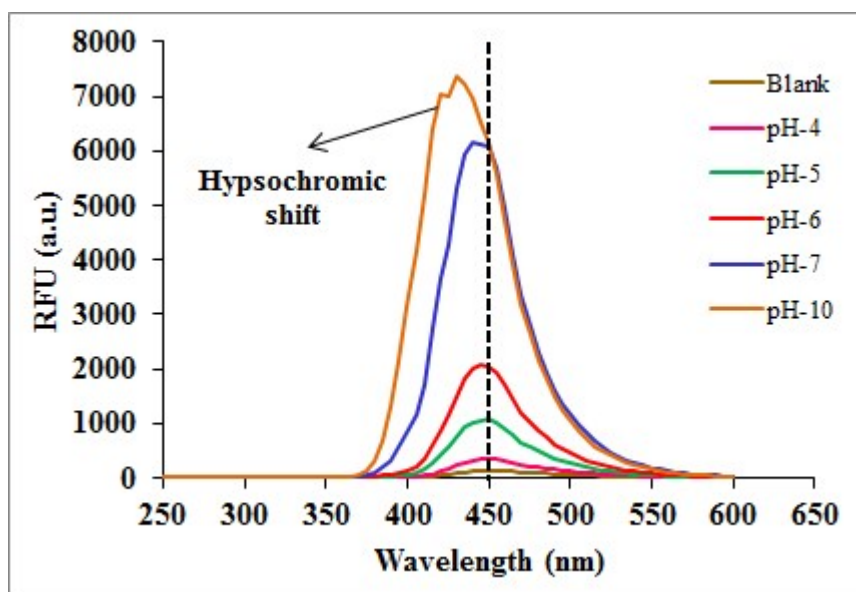
Figure S5. Fluorescent behaviour of Al-MOF at different pH.

a)

b)
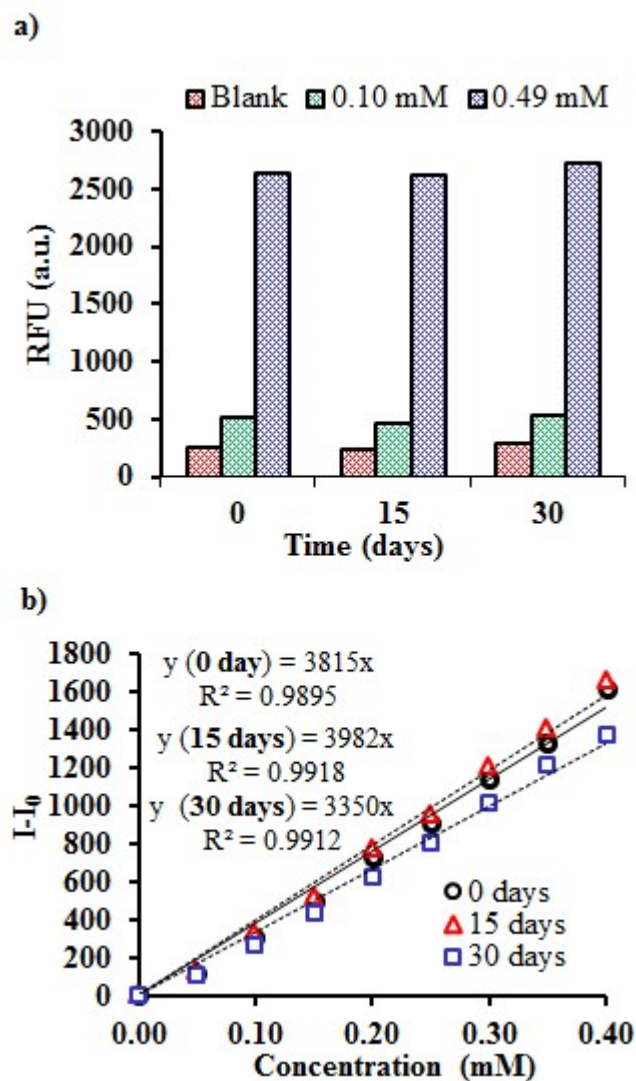
Fig. S6. Sensitive response of stored Al-MOF probe against TEA. a) Response of a month stored Al-MOF towards 0.1 and 0.49 mM of TEA concentrations and b) linear calibration curve of Al-MOF stored at different intervals against TEA
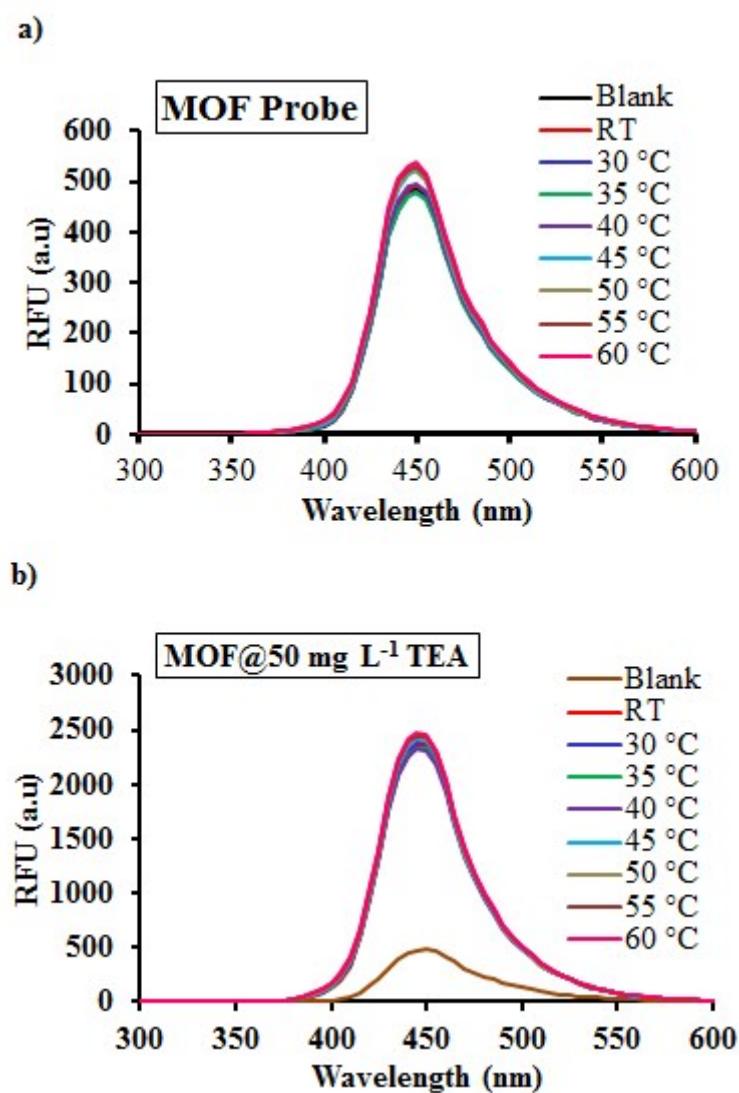
Fig. S7. Effect of temperature for the sensing of TEA using Al-MOF as a probe material.
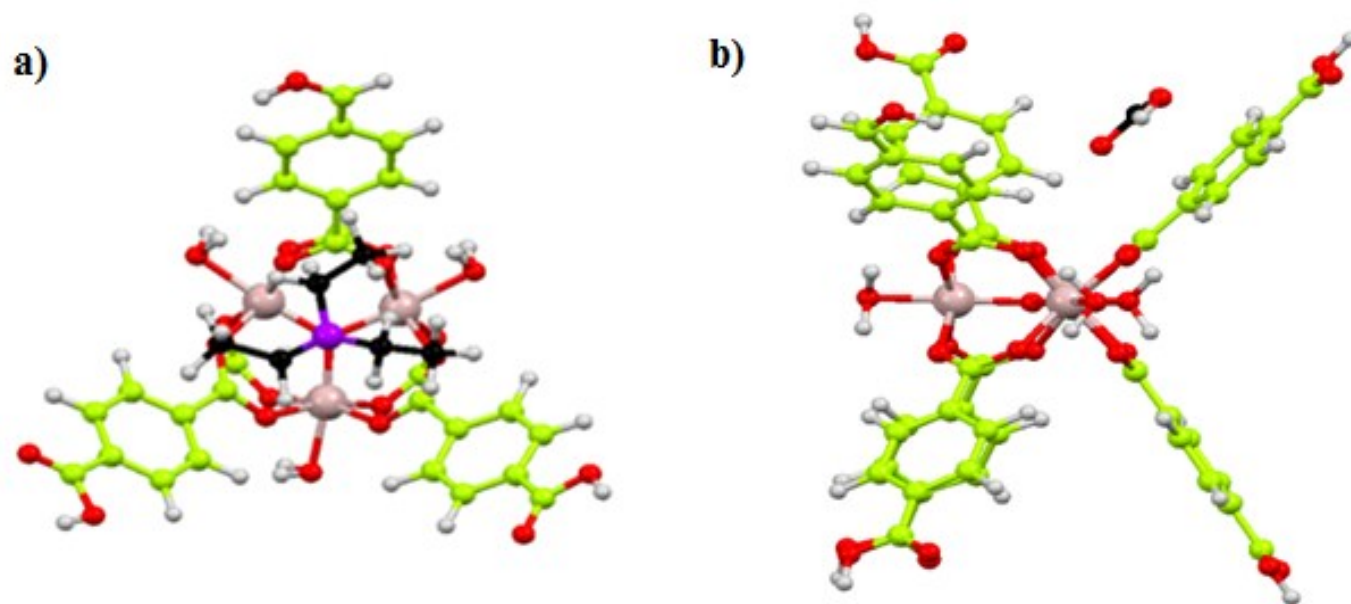
Fig. S8. Optimized atomic unit structure of Al-MOF with adsorbed TEA (a) and FA molecules (b). Note: carbon atoms of TEA were highlighted by black colour.
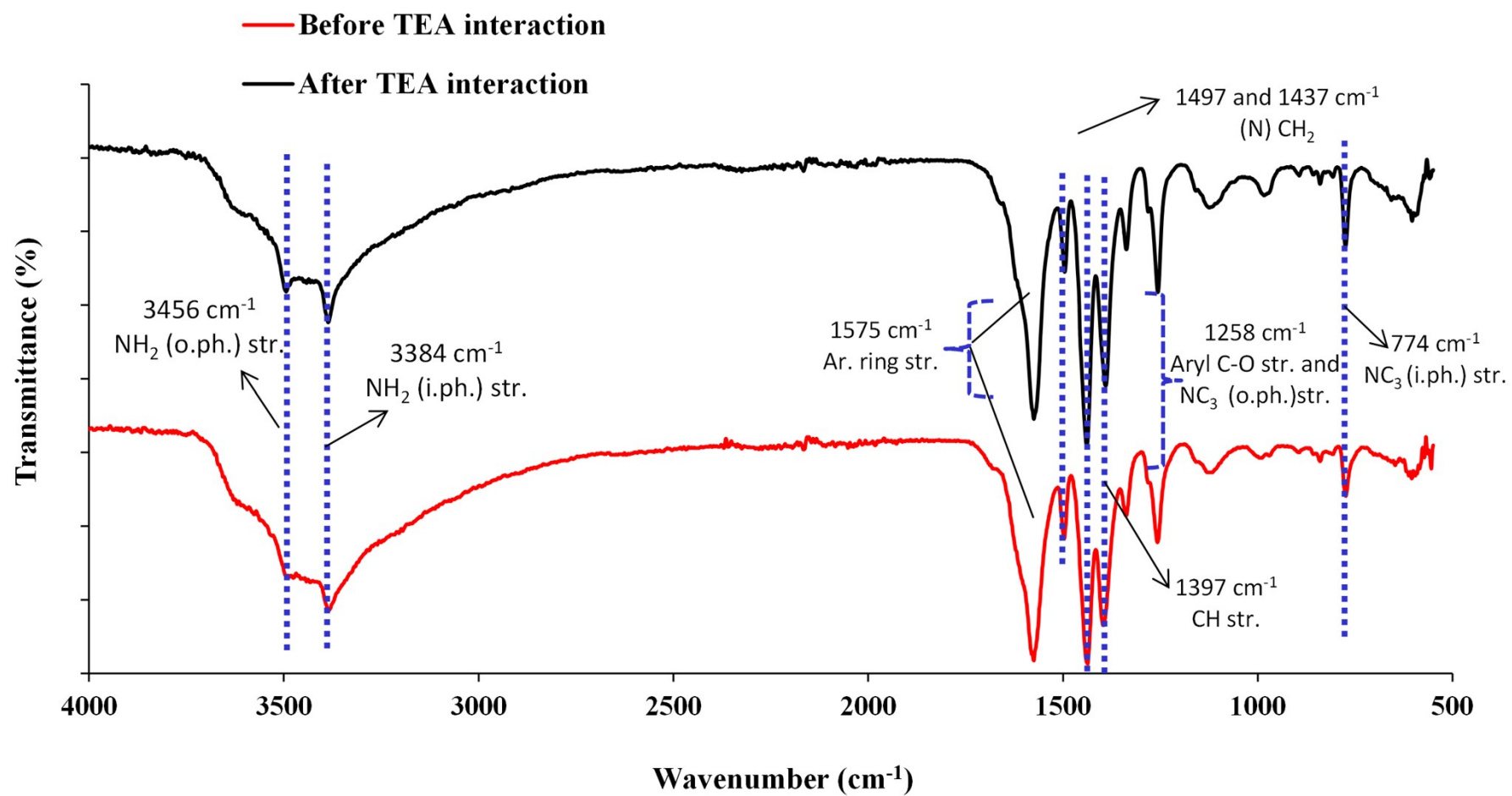
Fig. S9. FTIR results of Al-MOF before and after interaction with TEA.
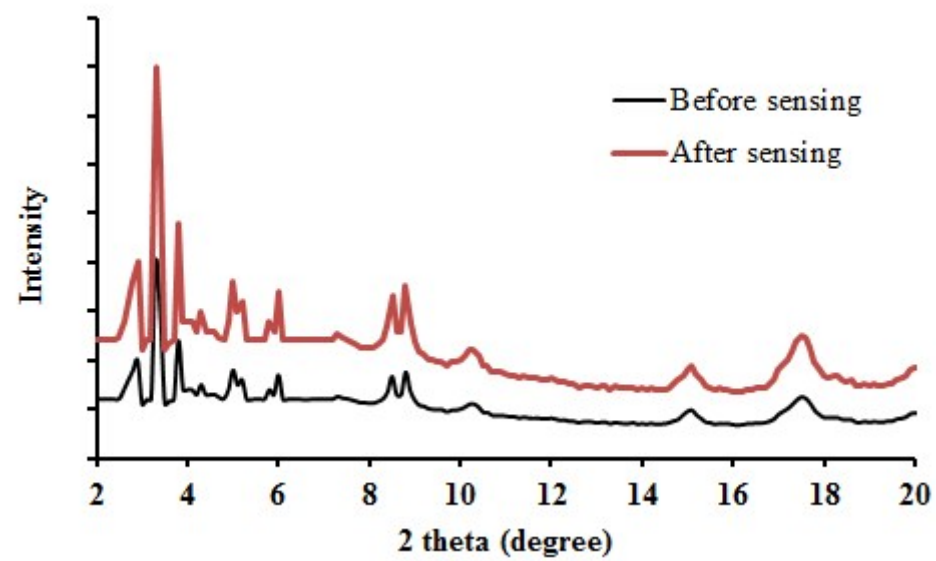
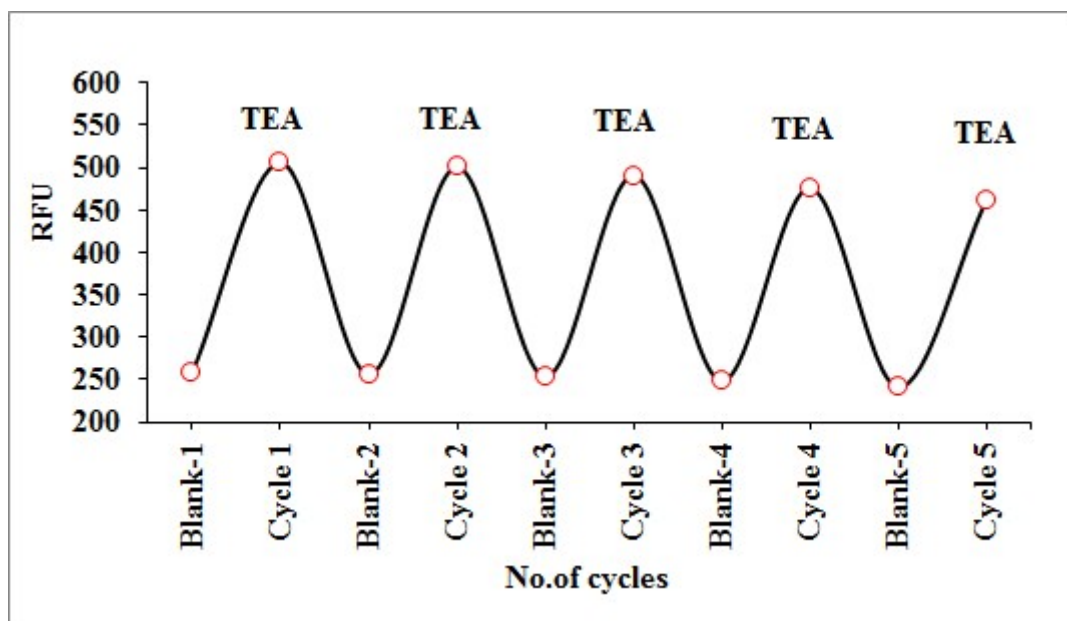**Fig. S10.** PXRD results of Al-MOF before and after interaction with TEA

Fig. S11. Regeneration profiles of Al-MOF after interaction with TEA. (Concentration of TEA: 0.10 mM, desorbing agents: water and ethanol in 1:1 ratio and thermal treatment (150 °C for 2 h).