

Supporting Information

pH-Triggered Adjustable Bursting of Liquid Marbles on Water Pool

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Experimental Section:

Materials:

2-Aminoterephthalate (H₂ATA), zirconium chloride (ZrCl₄), trimethylolpropane triacrylate (3-Acl; molecular weight: 296.31 g/mol), butyl amine, pentyl amine, hexyl amine, octyl amine, decyl amine, sulfanilamide, aniline, rhodamine B, potassium thiocyanate, Iron(III) chloride hexahydrate, sodium dodecyl sulphate (SDS), methylene blue and DMSO-*d*₆ were purchased from Sigma Aldrich (Bangalore, India). DMF was purchased from Alfa-Aesar, India. Sodium hydroxide, sodium chloride, sodium nitrite and hydrochloric acid were purchased from Emparta (Merck Specialties Private Limited). Superglue (Ethyl Cyanoacrylate) was procured from Amazon India. Ethanol and methanol were purchased from Changshu Hongsheng Fine Chemical. Microscopic glass slides were purchased from JSGW (Jain Scientific Glass Works), India. Milli-Q grade water was used for all experiments.

General Considerations:

The contact angle measurements were performed using KRUSS Drop Shape Analyser-DSA25 instrument with an automatic liquid dispenser at ambient conditions. Static contact angles were measured at four different positions for each sample. Field Emission scanning electron microscope (FESEM) images were taken using Sigma Carl Zeiss scanning electron microscope (a thin layer of gold coating was done on the sample prior to the imaging). UV-Vis spectra for transmittance measurement were recorded using the Perkin-Elmer Lambda 750 (UV/Vis/NIR Spectrometer). The ¹H NMR spectra were recorded using Bruker 500 MHz NMR spectrometer. For the ¹H NMR analyses of MOFs, 5 mg of sample was dispersed in 10 μL of HF, followed by adding 500 μL of DMSO (*d*₆) to dissolve the sample under sonication. Transmission electron

microscope images were obtained using JEOL-2100F Field Emission Transmission Electron Microscope (FETEM). The Attenuated Total Reflectance Spectra was recorded using a PerkinElmer ATR instrument at ambient conditions in the range of 400-4000 cm^{-1} . Nitrogen adsorption-desorption measurement was carried out by Quantachrome Autosorb-IQ MP gas sorption analyzer at 77 K. X-ray powder diffraction patterns of the samples were recorded by using a Rigaku Smart Lab X-ray diffractometer using $\text{Cu-K}\alpha$ ($\lambda=0.15406$ nm) radiation at 9 kv (50kv, 100 mA) with a 1D detector (scan speed: 0.05 degree/second). Digital pictures were captured using a canon power shot SX420 IS digital camera.

Synthesis of $\text{NH}_2\text{-UiO-66}$:

$\text{NH}_2\text{-UiO-66}$ was synthesized by following the previously reported methods with minor modifications.¹ Sequentially, H_2ATA (0.186 g, 1.029 mmol) and ZrCl_4 (0.240 g, 1.029 mmol) were dissolved in 60 mL of anhydrous DMF, followed by the addition of 0.2 mL of deionized water into the solution. The resulting solution was stirred at room temperature for 5 min and then transferred to 100 mL Teflon-lined autoclave. The reaction was carried out at 120 °C for 24 h, giving rise to a suspension that was later filtered and washed with DMF and acetone, and dried under vacuum condition to obtain the yellowish product. The product was characterized by ^1H NMR. The ^1H NMR data for MOF (DMSO-d_6 , 500 MHz): δ = 7.77 (d, J = 8.2 Hz, 1H), 7.38 (s, 1H), 7.03 (d, J = 8.2 Hz, 1H).

Synthesis of Chemically Reactive MOF and Post modification:

$\text{NH}_2\text{-UiO-66}$ (117 mg, ca. 0.4 mmol eq. of NH_2) and 3-Acl (477 mg, 1.6 mmol, 4 eq.) were taken in a Teflon-lined autoclave containing 10 mL of ethanol. The autoclave was then sealed and heated at 120 °C for 48 h. After cooling to room temperature, the autoclave was opened and the yellow powder was thoroughly rinsed and periodically centrifuged with ethanol (20mL \times 3). After centrifugation of the resulting mixture, the powder was dried at 80 °C in an oven. For further modification, this powder was activated at 120 °C for 12 h. The product was characterized by ^1H NMR. The ^1H NMR data for CR-MOF (DMSO-d_6 , 500 MHz): δ = 7.87 (d, J = 8.2 Hz, 2H), 7.27 (s, 2H), 7.10 (d, J = 8.2 Hz, 2H), 6.25 (dd, J = 17.2, 1.6 Hz, 1H), 6.07 (dd, J = 17.2, 10.3 Hz, 1H), 5.87 (dd, J = 10.3, 1.6 Hz, 1H), 3.49 (t, J = 6.5 Hz, 2H), 3.45 (t, J = 6.6 Hz, 2H), 2.73 – 2.70 (m, 2H), 2.63 (t, J = 6.4 Hz, 2H), 2.57 (t, J = 6.4 Hz, 2H), 1.17 (t, J = 7.1 Hz, 3H).

Post modification of CR-MOF with alkyl amines:

Activated CR-MOF (100 mg) and 1 mL of different alkyl amines (butyl amine, pentyl amine, hexyl amine, octyl amine and decyl amine) solutions were taken separately and stirred overnight at ambient condition. After completion of the reaction, the resultant mixtures were centrifuged 3 times with 20 mL of ethanol each to remove the residual amines. Next, the products were dried in an oven at 80 °C prior to use it in various characterizations and demonstrations. The ^1H NMR data for pentyl amine modified CR-MOF: ^1H NMR (DMSO-d_6 , 500 MHz): δ = 7.87 (d, J = 8.2 Hz, 2H), 7.27 (s, 2H), 7.10 (d, J = 8.2 Hz, 2H), 3.49 (t, J = 6.5 Hz,

2H), 3.45 (t, $J = 6.6$ Hz, 2H), 3.10 (t, $J = 6.3$ Hz, 2H), 2.91–2.87 (m, 2H), 2.74–2.69 (m, 2H), 2.63 (t, $J = 6.3$ Hz, 4H), 2.57 (t, $J = 6.3$ Hz, 2H), 1.57–1.50 (m, 2H), 1.32–1.25 (m, 4H), 1.17 (t, $J = 7.1$ Hz, 3H), 0.87 (t, $J = 6.6$ Hz, 3H).

Surface morphology of MOFs liquid marble: The surface structure of the selected MOFs liquid marbles were characterized with FESEM imaging. To observe the MOFs liquid marbles, MOFs liquid marbles were exposed to ECA vapor at 50 °C to cause anionic polymerization at the air–water interface of the MOFs liquid marble.

Lifetime analysis of MOFs liquid marble on water pool: To study the lifetime of liquid marbles of different amine modified CR-MOF on a water pool, the freshly prepared liquid marbles of DI water (20 μ L) were gently placed on a water pool with the help of a metal spatula. Digital images were acquired at regular intervals to study the lifetime of the LMs.

Impact test for MOFs liquid marble: The impact test was performed by dropping a liquid marble of volume 10 μ L from a certain height to study the breakage behavior of the liquid marbles.

Compression test for MOFs liquid marble: The liquid marbles were prepared of different amine modified CR-MOF were subjected to controlled and repetitive compressive strains. In this context, a lab-made setup was built to apply gradual compressive strain on the prepared liquid marbles. Two clean microscopic glass slides were attached to the upper and lower platforms of a laboratory jack. Then, respective liquid marble was gently placed on the lower glass slide, prior to gradually bringing down the upper glass slide to apply gradual compressive strain on the liquid marble by rotating the attached screw of the laboratory jack. The compressive strain was calculated by measuring the change in the height of the respective liquid marble before and after its deformation. Further, this experimental setup was utilized to apply compressive strain of 50% repeatedly. Further, the liquid marbles were also compressed with bare finger, where the liquid marble was placed on a finger and pressed repeatedly using the thumb for several times.

Liquid marbles fabrication and its acid/alkaline triggered bursting:

A droplet of water was individually beaded on a pile of different amine modified CR-MOF powder. After the droplet was rolled over, chemically modified superhydrophobic/hydrophobic MOF particles spontaneously self-organized to encapsulate the water droplet to form the liquid marble (LM). The different amine modified liquid marbles were transferred into a petri dish containing 50 mL of water divided superficially into four sections. Then, 415 μ L of concentrated HCl was added to the center of the petri dish to make the water solution of pH 1. In another setup, 400 μ L of NaOH (0.2 μ M) solution was separately added to the center of another petri dish to make the water solution of pH 12. Both in pH 1 and pH 12, the liquid marble of pentyl amine modified hydrophobic MOF was found to burst,

followed by the liquid marble of hexyl amine modified MOF, but the liquid marbles of octyl and decyl amine modified MOF remained intact. See the main text for more details.

Triggered chemical reaction on air/water interface:

Two different liquid marbles of pentyl amine modified hydrophobic MOF were prepared using aqueous solutions (20 μ L) of mutually reactive reactants, i.e. potassium thiocyanate (one equivalent) and iron(III) chloride (nine equivalent, 57 mM) solution. Similarly, another two distinct liquid marbles of decyl amine modified superhydrophobic MOF were to encapsulate above mentioned aqueous solutions of potassium thiocyanate and iron (III) chloride. A petri dish containing 50 mL of water was divided superficially into two parts (see main text for more details) prior to transfer these liquid marbles, where two LMs of decyl amine modified MOF were placed on the left half of the water pool and other portion of the air/water interface accommodated two LMs of pentyl amine modified MOF. On addition of aqueous droplet of acid to the water pool, the liquid marbles of pentyl amine modified MOF popped out—and the mutually reactive released reactants formed metal complex to give a visually distinguishable red color. However, the liquid marbles of decyl amine modified MOF remained intact to their shape—and failed to release encapsulated reactants at identical setting.

Drug releasing behavior of liquid marble in acidic, neutral and basic condition: The release of rhodamine-B from different liquid marbles in distinct pH circumstance, that was individually prepared from pentyl amine and hexyl amine modified MOF were studied by measuring the change in UV-absorption intensity at λ_{max} in the aqueous phase. In this context, rhodamine-B solution (1 mg/mL solution) was prepared in de-ionized water. The pentyl amine and hexyl amine modified CR-MOF were separately used to form respective liquid marble encapsulating the aqueous solution of rhodamine B. The dye loaded liquid marble was subsequently placed on an acidic, neutral and basic water pool to examine the release of rhodamine B by visual inspection and UV spectral analysis. The aqueous aliquot was collected at different time intervals to obtain the UV absorption spectra. The UV/Vis absorption of the collected aliquots at regular intervals was recorded with the Perkin-Elmer Lambda 750 UV/Vis/NIR Spectrometer to get the percentage of change in intensity of UV-absorption in the water pool due to the release of rhodamine B.

Sensing of Nitrite ion:

A 20 μ L droplet of solution of sulfanilamide (1 mM), aniline (1 mM) rolled on a pile of pentyl amine modified CR-MOF powder. After the droplet was rolled over, chemically modified hydrophobic MOF particles spontaneously self-organized to encapsulate the solution of sulfanilamide (1 mM), aniline (1 mM) to form the liquid marble (LM). The pentyl amine modified liquid marbles were transferred into a petri dish containing 20 mL of water without and with Nitrite (40 μ L) solution. Then, 170 μ L of concentrated HCl was added to the corner of the petri dish to alter the pH of water pool to pH 1. After addition of acid the liquid marble

of pentyl amine modified hydrophobic MOF was found to burst in both case but water pool containing nitrite, turns yellow to form diazo dye, however without nitrite, it didn't show any colouration. See the main text for more details.

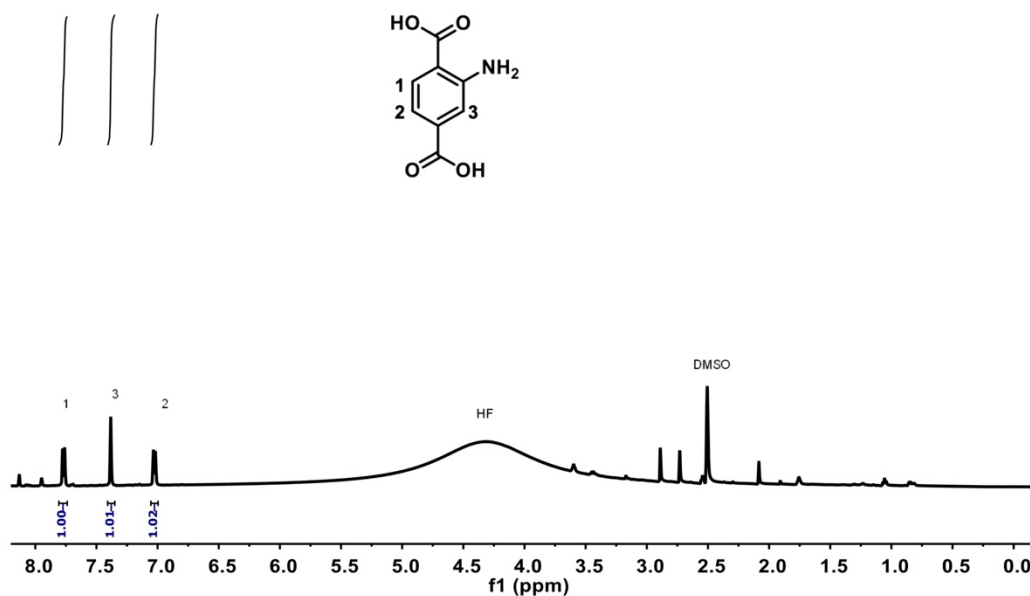


Figure S1. ^1H NMR spectra of $\text{NH}_2\text{-UiO-66}$ MOF was digested/ dissolved in HF/ $\text{DMSO-}d_6$ (10 μL + 500 μL).

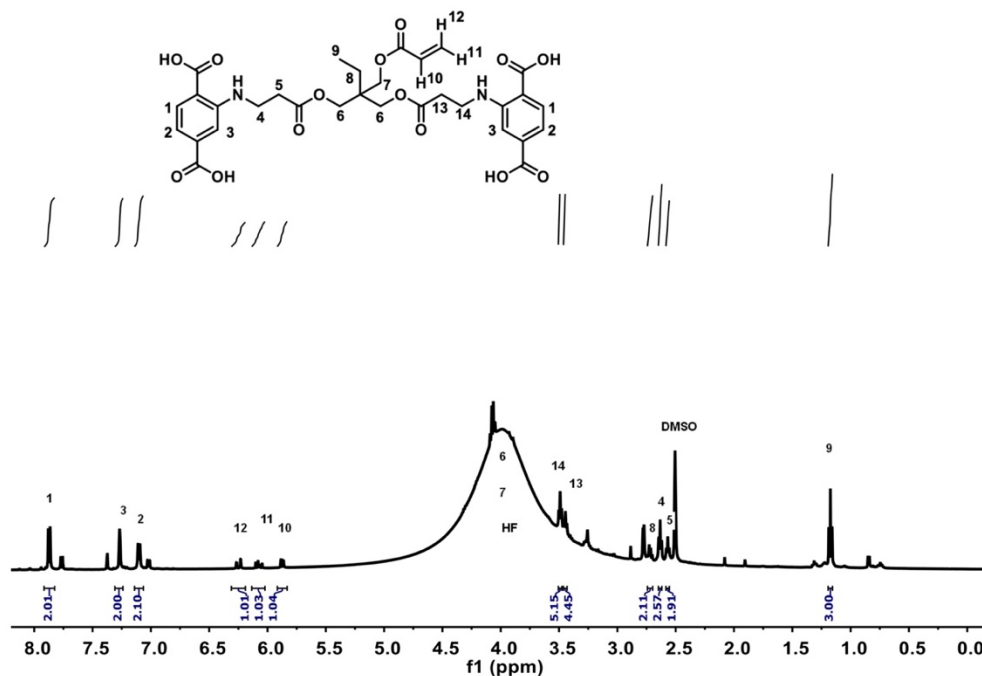


Figure S2. ^1H NMR spectra of 5 mg of chemically reactive MOF was digested/ dissolved in HF/ $\text{DMSO-}d_6$ (10 μL + 500 μL).

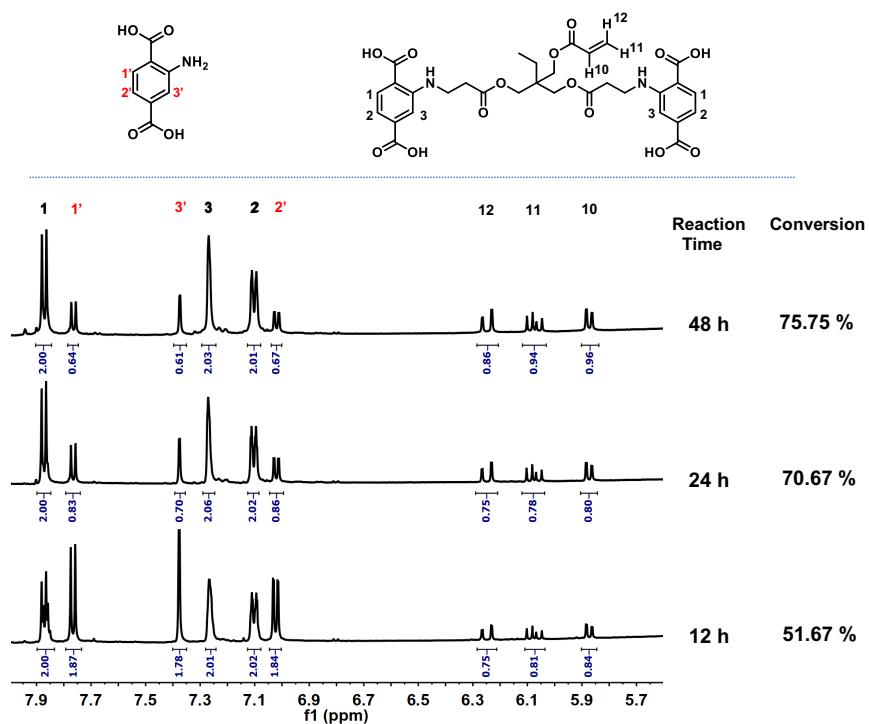


Figure S3: ¹H NMR spectra of 5 mg of chemically reactive MOFs were digested/ dissolved in HF/ DMSO-*d*₆ (10 μL + 500 μL), where reaction duration between NH₂- UiO-66 MOF and 3AcI was varied from 12h to 48 h.

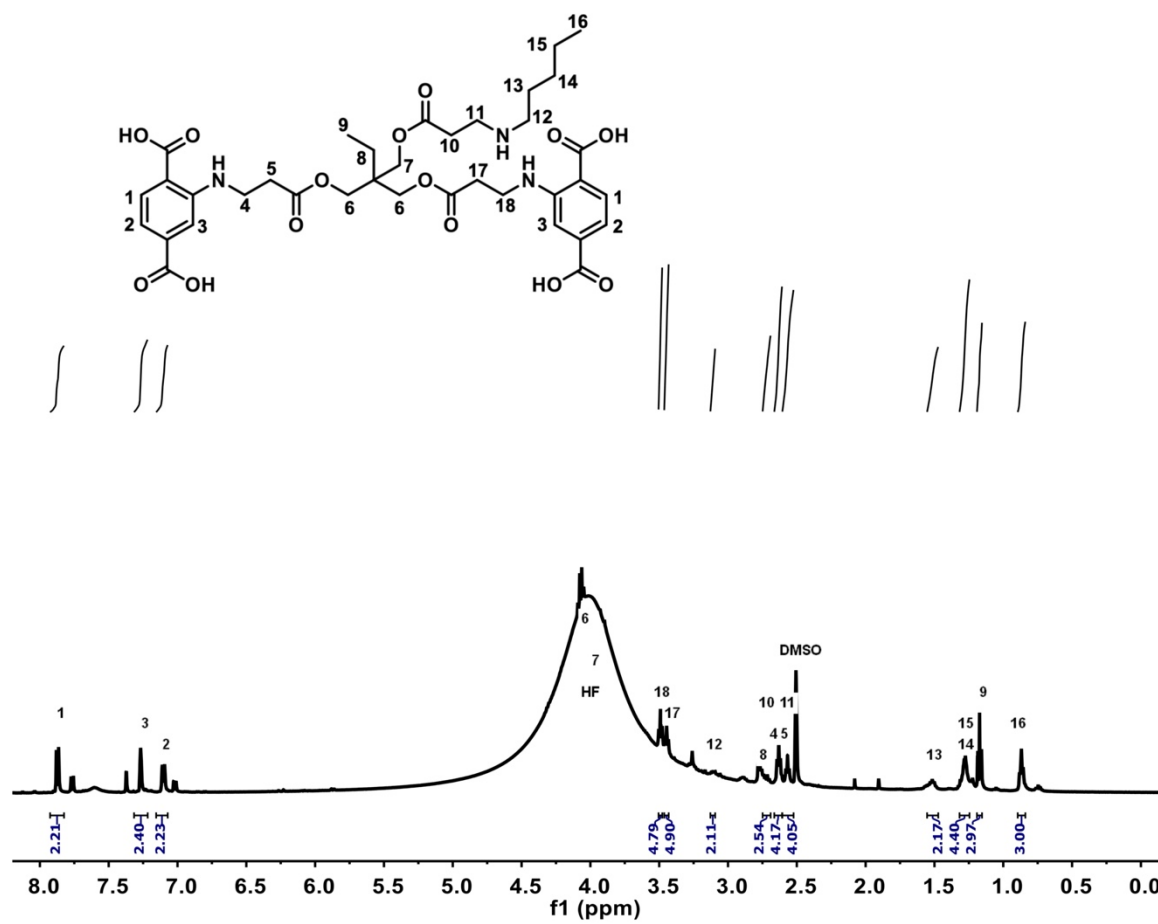


Figure S4. ^1H NMR spectra of pentylamine (PA)-modified MOF was digested/ dissolved in HF/ DMSO- d_6 (10 μL + 500 μL).

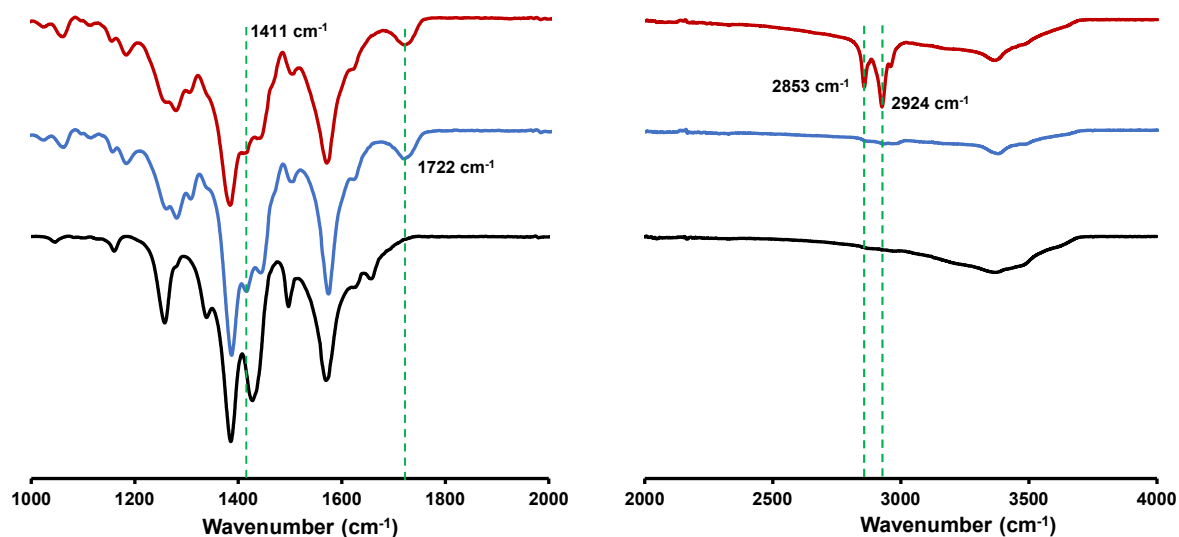


Figure S5. FTIR spectra of NH₂-UiO-66MOF (black) and CR-MOF before (blue) and after (PA@3AcI@NH₂-UiO-66MOF; red) postmodification with pentylamine.

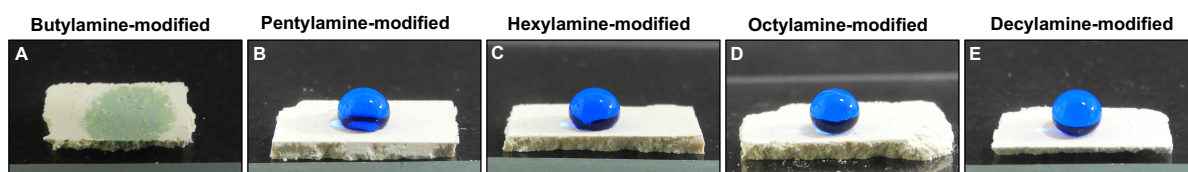


Figure S6 : A-E) Digital images accounting the wettability of beaded water droplet (blue color aids visual inspection) on the prepared MOFs that were individually post modified with different alkyl amine—including butyl amine (A), pentyl amine (B), hexyl amine (C), octyl amine (D), and decyl amine (E).

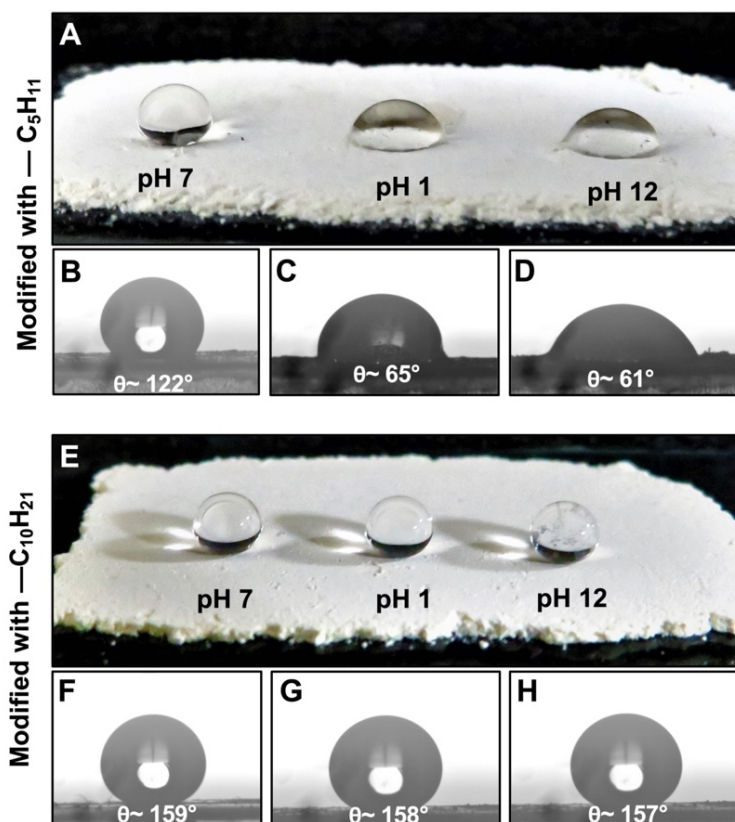


Figure S7. Digital (A and E) and contact angle (B-D and F-H) images of beaded droplet of neutral water (pH 7), acidic water (pH 1) and alkaline water (pH 12) on the pentyl amine and decyl amine-modified MOFs.

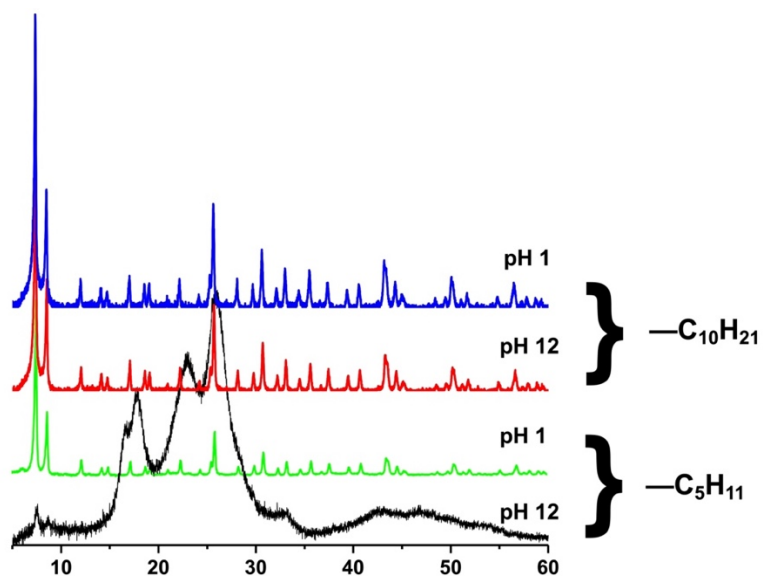


Figure S8. Powder XRD pattern of pentyl amine and decyl amine modified MOF in highly acidic (pH 1; green and blue) and alkaline (pH, 12; black and red) conditions.

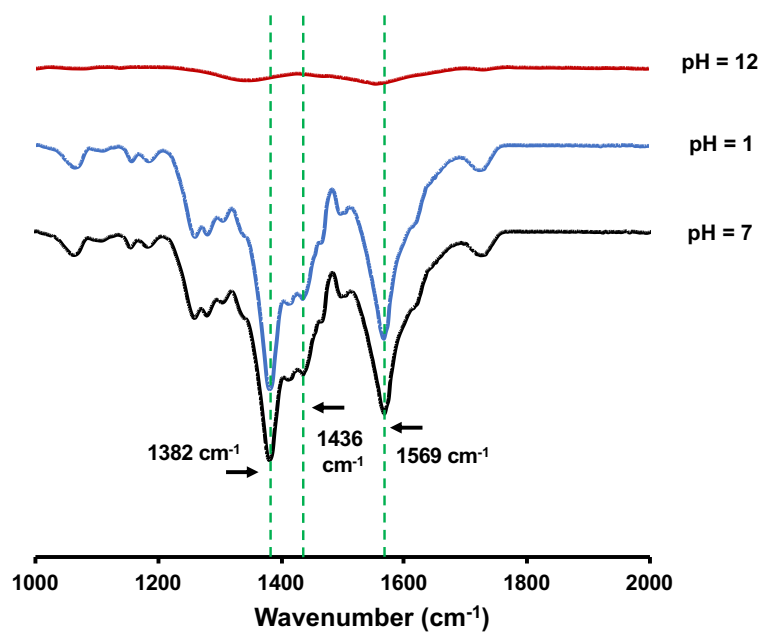


Figure S9: FTIR spectra of modified MOF after exposure to alkaline (pH 12, red), acidic (pH1, blue) and neutral (pH 7, black) water.

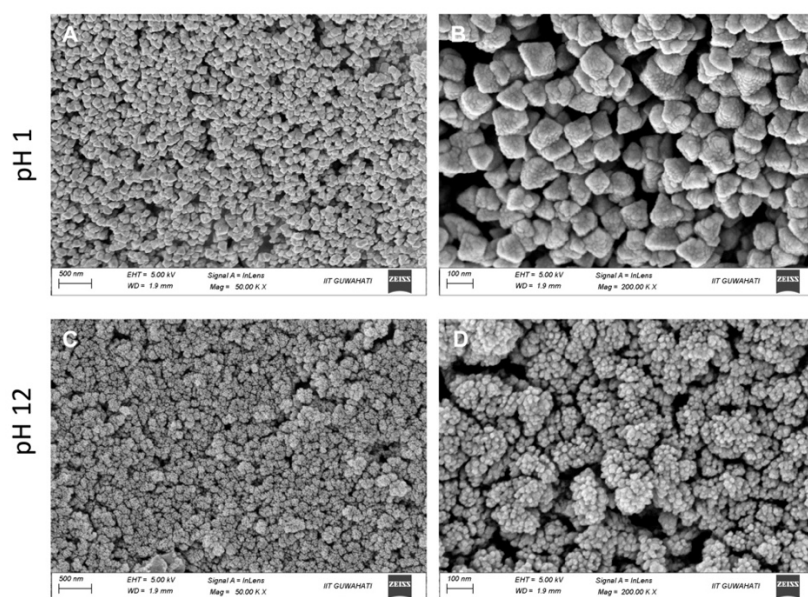


Figure S10. SEM images of pentyl amine modified MOF after exposure to acidic (A and B) and basic condition (C and D) in both lower (A,C) and higher (B,D) magnifications.

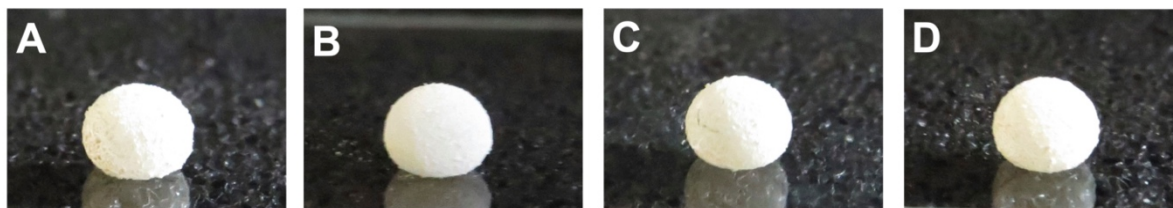


Figure S11. Digital images of liquid marbles that were derived from pentyl amine (A), hexyl amine (B), octyl amine (C), and decyl amine (D)-modified MOFs.

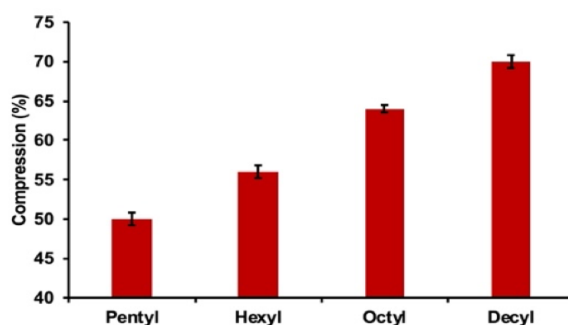


Figure S12. The plot compares the limit of tolerance LMs for sustaining the applied compressive strains. See the Movie 1 for more details.

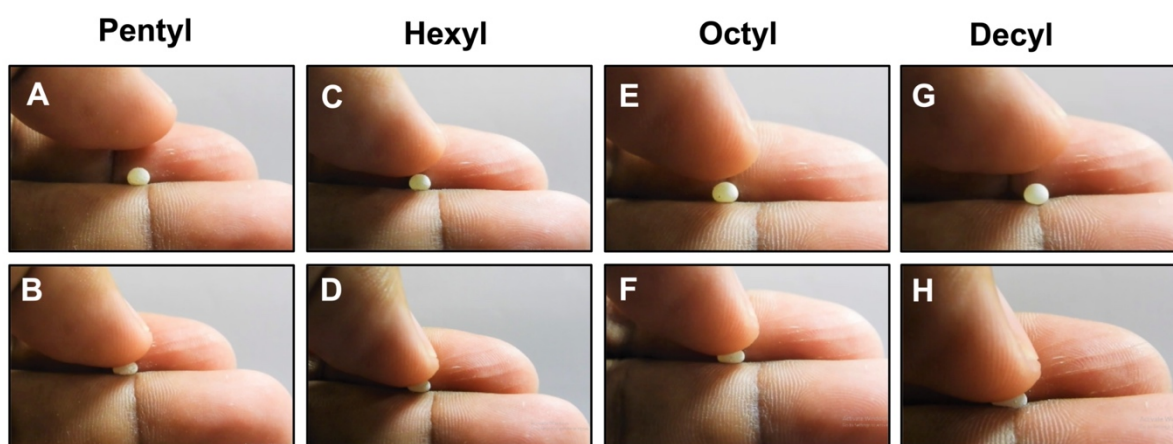


Figure S13. Digital images of liquid marbles of different alkyl amine modified MOFs [Pentyl (A-B), Hexyl (C-D), Octyl (E-F), and Decyl (G-H)] while compressing with bare hand.

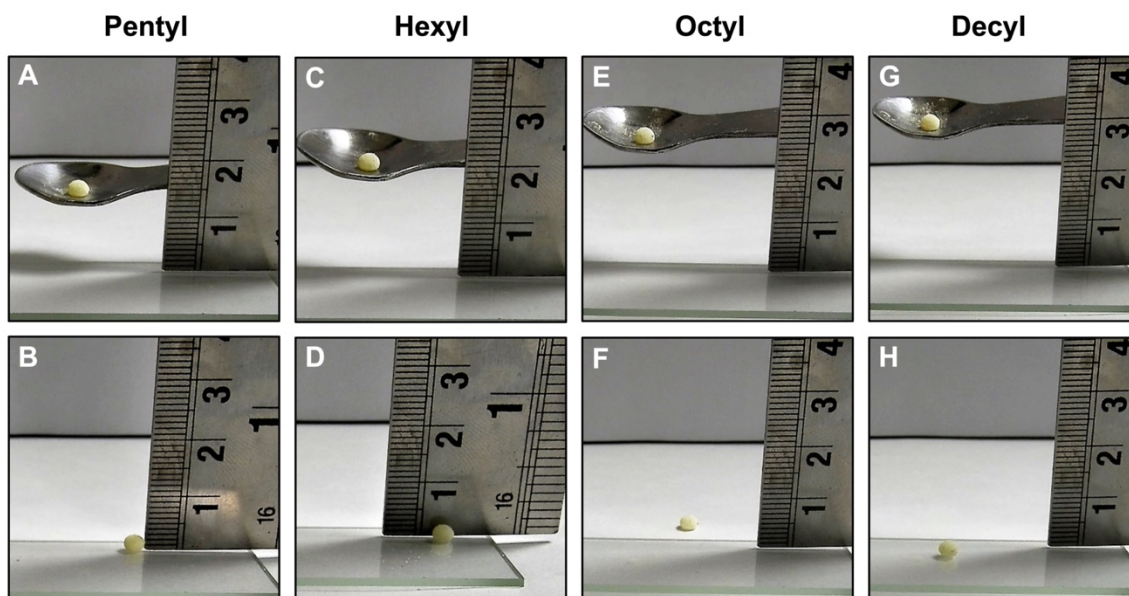


Figure S14. Digital images of different alkyl amine modified liquid marbles [Pentyl (A-B), Hexyl (C-D), Octyl (E-F), and Decyl (G-H)] before and after dropping from different heights.

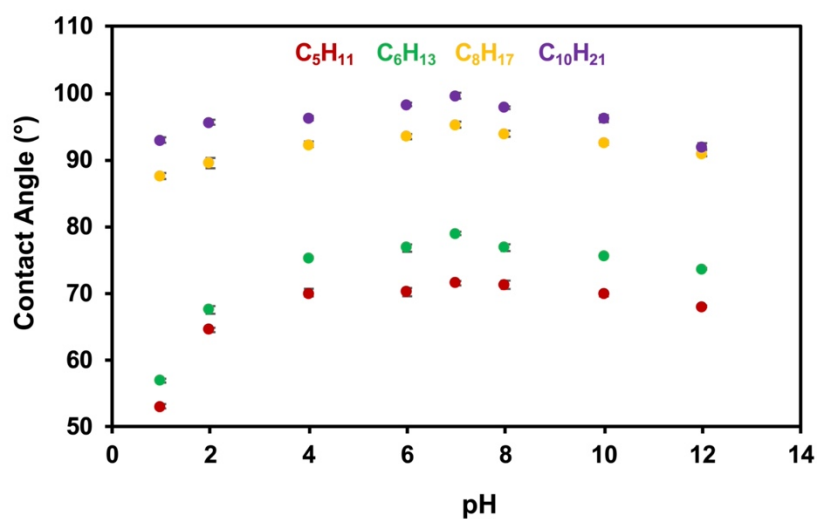


Figure 15. Plot showing the change in the Young contact angle of a beaded aqueous solution of different pH on different coatings on flat substrates, where 3Acl and different selected alkyl amines were used individually to apply the coating on glass substrate before measuring the contact angle.

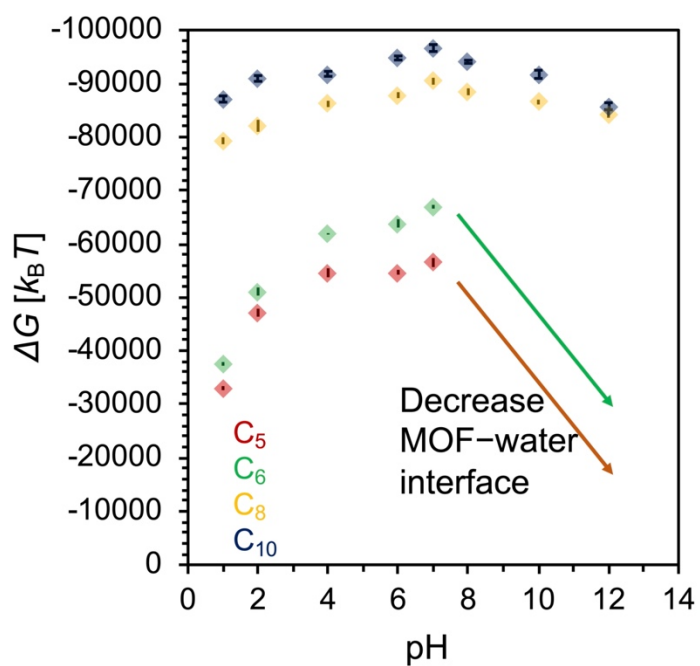


Figure 16. The plot accounting for the change in adsorption energy of chemically modified MOF to aqueous surface with variation of pH.

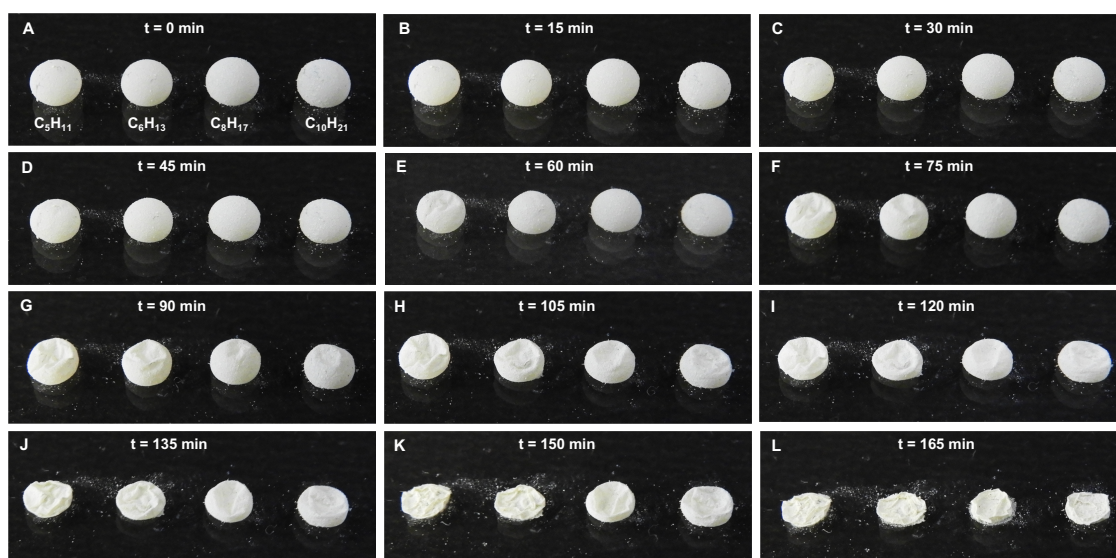


Figure S17: Digital images accounting for the stability of the LMs (prepared from differently modified MOFs) on solid surface. No release of liquid water was noticed, rather, inner water was evaporated out and resulted in buckling of the LMs over the time.

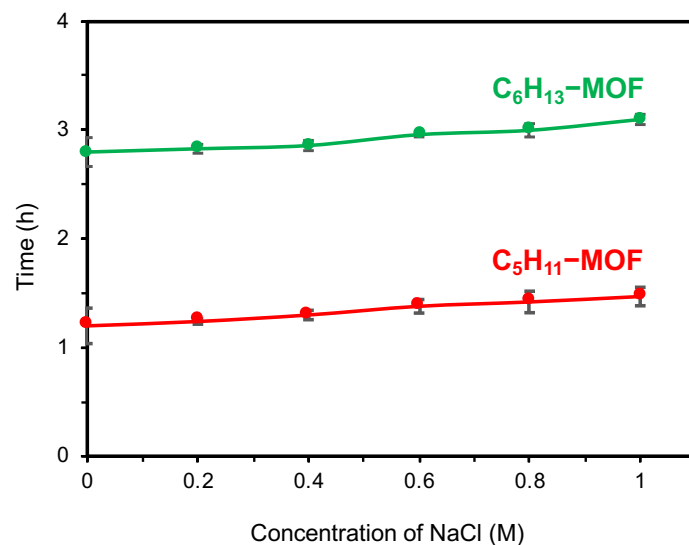


Figure S18. Accounting a slight improvement in lifetime of liquid marbles (hexyl and pentyl modified MOF based LMs) with increasing the ionic strength of the water pool, where concentration on NaCl was gradually increased to enhance the ionic strength of water pool.

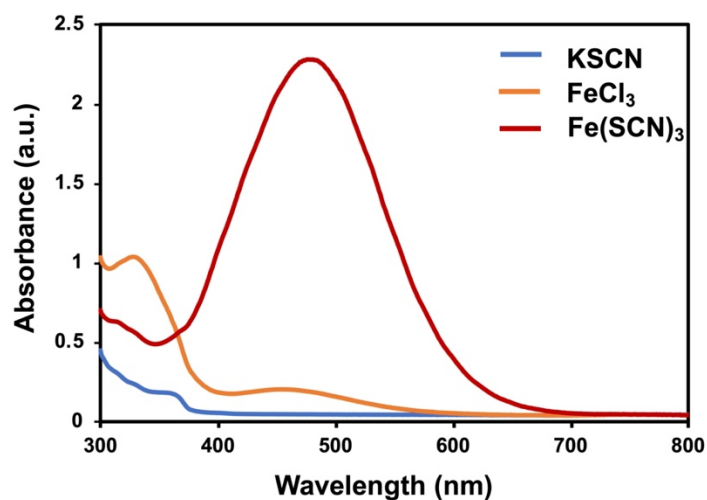


Figure S19. UV-Vis absorbance spectra of $FeCl_3$ and KSCN and $Fe(SCN)_3$ in HCl(1M) solution.

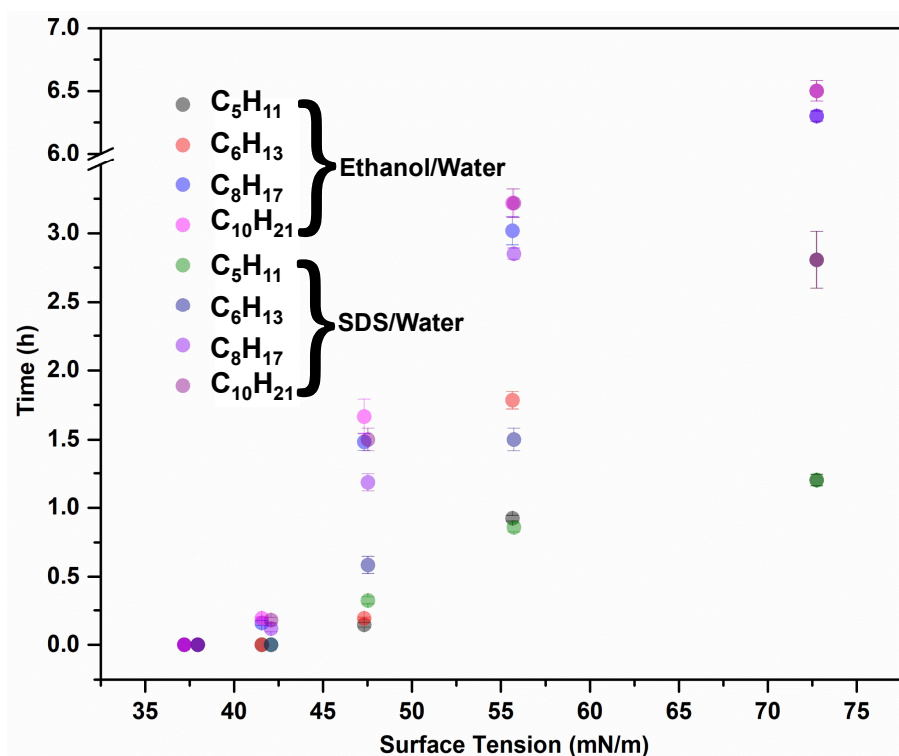


Figure S20. The plot accounting for the lifetime of the prepared LMs on water pool where liquids with different surface tension were used to prepared the LMs.

Reference.

1. D. Sun, P. R. Adiyala, S.-J. Yim and D.-P. Kim, *Angew. Chem. Int. Ed.*, 2019, **58**, 7405–7409.