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Supporting Information

Alkali Metal-ion Assisted Michael Addition Reaction in Controlled Tailoring of Topography in Superhydrophobic Polymeric Monolith

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Materials: Branched poly (ethyleneimine) (BPEI, MW~25000), dipentaerythritol Pentaacrylate (5Acl, MW~ 524.21) were purchased from Sigma Aldrich (Bangalore, India). Propylamine, pentylamine, hexylamine, octylamine, decylamine (DA) were purchased from Sigma Aldrich (Bangalore, India). Absolute ethyl alcohol (CAS Registry No. 64175, Lot 17030799) was procured from TEDIA Company (United Sates of America). Microscopic glass slides were obtained from JSGW (Jain Scientific Glass Works) India. Dichloromethane (DCM) and chloroform was obtained from Merck Life Science Private Limited, Mumbai, India. Reagent grade THF was purchased from RANKEM (Maharashtra, India). Adhesive tape was purchased from Jonson Tapes (India). Rhodamine-6G was purchased from Labo Chemie (Laboratory Reagents and Fine Chemicals, Mumbai, India). Methylene blue was obtained from Sigma Aldrich (Bangalore, India). NaOH was obtained from Emparta (Merck Specialties Private Limited). HCl was purchased from Fischer Scientific, Mumbai, India. River water was collected from Brahmaputra River in Guwahati (Assam, India). Sand grains were collected from a local construction site at IIT Guwahati and was rinsed thoroughly prior to use. All materials were used as obtained without any further purification.

General Considerations:

Glass vials used for preparation of various solutions were thoroughly washed with acetone and ethanol prior to use. Field emission scanning electron microscope (FESEM) images were acquired using Sigma Carl Zeiss Scanning electron microscope. Samples were coated with a thin layer of gold after mounting on a double sided carbon tape. FTIR spectra were recorded at ambient conditions using PerkinElmer instrument and samples were grinded with KBr to prepare pellets for analysis. Dynamic light scattering

(DLS) study was performed using Zetasizer Nano ZS90 instrument (Model No. ZEN3690). The contact angles were obtained using Kruss Drop Shape Analyser-DSA-25 instrument at ambient conditions. Advancing and receding contact angles were measured using deionized water droplet at four different locations for each sample. Mechanical property was analyzed for the polymeric material (2 cm × 1 cm × 1 cm) that are synthesized in presence of various alkali metal salts including LiCl, NaCl, KCl, RbCl and CsCl using universal testing machine (Instron 5944, Norwood, MA, U.S.A.). Digital images were acquired using a canon power shot SX420 IS digital camera.

Computational Methodology: Geometries of all the considered reactants, transition states and products were fully optimized at DFT level using B3LYP/6-311++G(2d,2p) and B3LYP/6-31++G(d,p) methods on Gaussian 09 program package.[1] LANL2DZ, a double-ζ quality basis set, was used for Rb^+ and Cs^+ metal ions. Frequency calculations at the optimization levels characterize the obtained stationery points as minima or transition state on the potential energy surface. Intrinsic reaction coordinate (IRC) calculations were carried out, at the optimization levels, in forward and reverse directions to validate the reaction path and to follow the reaction profile.[2] Natural bond orbitals (NBO) calculations were carried out at B3LYP/6-31++G(d,p) level to estimate the NBO based atomic charges and charge transfer details.[3] The effect of ethanol solvent was included in all the calculations using integral equation formulation of the polarizable continuum model (IEF-PCM) available in Gaussian 09 program package.

Preparation of Polymeric Material with Tailored Topography:

Before preparation of solution of respective reactants (BPEI, 5Acl), various alkali metal salts including LiCl, NaCl, KCl, RbCl and CsCl were separately dissolved in ethanol maintaining the desired molar concentrations. Then the Branched poly (ethyleneimine) (BPEI) and dipentaerythritol Penta/Hexaacrylate (5Acl) solutions were prepared separately by dissolving 1.325g of 5-Acl and 0.5g of BPEI in 10 mL of ethanol that is doped with different alkali metal salts. Next the 5-Acl and BPEI were mixed in definite proportions

(1 mL of 5Acl and 0.3 mL of BPEI) and was kept for shaking and allowed to form the polymeric gel material. The material that was prepared in presence of various alkali metal salt were taken time to form the gel and the topography of the material was also changed based on the selection of the alkali metal ions in the reaction mixture. The topography of the polymeric gel material were characterized with FESEM (see the main text for more details).

Tailoring of Water Wettability on Polymeric Material:

The Polymeric materials that are prepared in presence of different alkali metal salts were thoroughly washed with THF for one hour and was subsequently transferred in to primary amine containing selected small molecules—including hexylamine (30 mg/mL), octylamine (30 mg/mL) and decylamine (30 mg/mL) respectively and were kept them for overnight. Thereafter, the polymeric gel was rinsed with THF to remove the unreacted small molecules and was dried at ambient conditions and using vacuum. Subsequently, the water wettability property of the material was examined with digital images and contact angle measurement.

Physical and Chemical durability:

Various severe physical and chemical durability tests were performed on the as synthesized polymeric material (that are prepared in presence of LiCl and post modified with DA molecules) to ensure their utility at the practical settings. Detailed procedure is as follows:

Sand Paper Abrasion Test: Here in this durability test, one side of the sand paper was immobilized on the microscopic glass slide using adhesive tape and the other portion was exposed to the synthesized polymeric material with a load of 200g and was moved 5 cm back and forth multiple times. During this experimental process, some material was physically eroded in form of powder and deposited on the sand paper. Thereafter, the anti-wetting property on the physically damaged material and the eroded powdery material that coated on the sand paper was examined with digital images and contact angle measurements.

Adhesive Tape Test: In this test, one side of the adhesive tape was fixed on the microscopic glass slide and the other side was exposed to the as synthesized polymeric material with a load of 200g to improve the contact between the adhesive tape and the polymeric material. Then, the material was peeled off from the tape and some portion of the material was transferred to the tape. The newly exposed interface was examined with beaded water droplet and contact angle measurements.

Sand Drop Test: In this test, the polymeric material was immobilized on the microscopic glass slide and 100g of sand grains were poured on the material from the height of 20 cm. The physical integrity as well as the anti-wetting property of the material remains unaltered after continuous exposure to the sand particles, which is clearly evident from the digital images and contact angle measurements.

UV irradiation test: In this test, the polymeric materials were exposed to UV radiations at short (264nm) and long (385nm) UV wavelengths with continuous exposure for 30 days and the anti-wetting property was examined each after 24 hours with water contact angle measurements.

Chemical Durability Test: The polymeric material was exposed to various harsh chemical aqueous conditions including extremes of pH (2 and 12), high ionic strength (artificial sea water) and river (Brahmaputra Assam, India) water for 10 days. Then, the anti-wetting property of the material was examined with digital images and contact angle measurements. Artificial sea water was prepared by dissolving $MgCl_2$ (0.2265g), $MgSO_4$ (0.325g), NaCl (2.673g) and $CaCl_2$ (0.112g) in 100 mL of deionized water.

Oil/Water Separation: Here, the oils of density lighter (motor oil, silicon oil, vegetable oil) as well as heavier (chloroform) than water were separated by the polymeric monolith that was synthesized in presence of LiCl and post modified with decylamine molecules. For the demonstration of floating oil collection, droplets of light oils were placed on the air/water interface and then the polymeric material was exposed to the floating oil droplets and the floating oil phase was selectively absorbed by the polymeric material. To separate the heavier sediment oil under water, chloroform was used as a model oil and we placed 5 mL of chloroform in 20 mL of aqueous phase. Then, the polymeric material was used exposed to oil/water mixture and the sediment oil phase under water was selectively absorbed by the material. The same material was also used in gravity driven filtration of both heavy and light oils from respective oil/water mixtures. The polymeric monolith was used as filter in the lab-made prototype (see main text for more details).

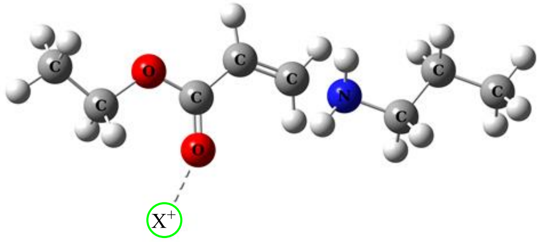
Reference:

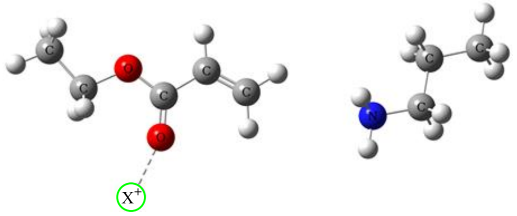
1. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

2. C. Gonzalez, H. B. Schlegel, J. Chem. Phys. 1989, 90, 2154-2161.

3. NBO 6.0. E. D. Glendening, J, K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison (2013).

Table S1: NBO charges on selected atoms in transition states and reactants

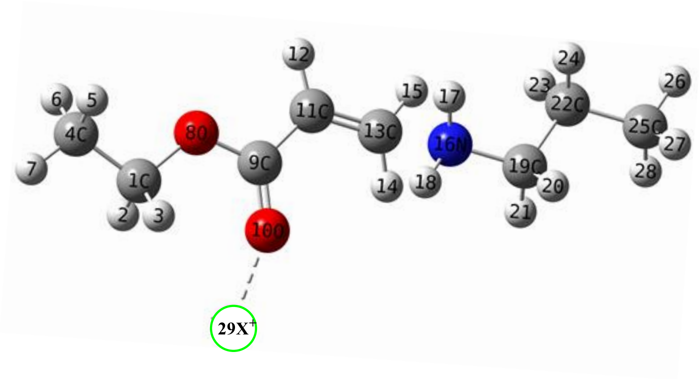




X^+	B3LYP/6-31++G(d,p) level				B3LYP/6-31++G(d,p) level			
	M	**O**	**N**	**C**	***M***	***O***	***N***	***C***
Li^+	0.991	-0.847	-0.747	-0.251	*0.993*	*-0.748*	*-0.940*	*-0.309*
Na^+	0.995	-0.823	-0.738	-0.255	*0.997*	*-0.719*	*-0.941*	*-0.319*
K^+	0.996	-0.808	-0.734	-0.256	*0.997*	*-0.704*	*-0.940*	*-0.321*
Rb+	0.997	-0.799	-0.731	-0.259	*0.998*	*-0.696*	*-0.941*	*-0.322*
Cs^+	0.998	-0.795	-0.729	-0.260	*0.999*	*-0.691*	*-0.940*	*-0.323*
None	-	-0.764	-0.720	-0.262	-	*-0.657*	*-0.937*	*-0.328*

X^+=Metal ions; 'M' shows charges on metal atom; 'O' shows charges on selected oxygen atom; 'N' shows charges on nitrogen atom; 'C' shows charges on selected carbon atom; NBO charges for reactants are depicted in italic texts

Table S2: The second-order perturbative estimates of donor-acceptor interactions in the NBO basis.



Donor NBO		Acceptor NBO		SE (kcal/mol)				
				Li^+	**Na^+**	**K^+**	**Rb^+**	**Cs^+**
LP(1)	O-8	LV(1)	X-29	0.16	0.15	0.09	0.06	-
LP(1)	O-10	LV(1)	X-29	2.44	0.54	0.28	0.06	-
LP(1)	O-10	RY(1)	X-29	0.06	0.06	0.33	-	-
LP(1)	O-10	RY(3)	X-29	0.45	-	0.06	-	-
LP(1)	O-10	RY(4)	X-29	0.05	-	0.09	-	-
LP(1)	O-10	RY(8)	X-29	0.12	-	0.1	-	-
LP(1)	O-10	RY(9)	X-29	0.08	-	-	-	-
LP(1)	O-10	RY(11)	X-29	0.05	-	-	-	-
LP(1)	O-10	RY(17)	X-29	0.09	-	-	-	-
LP(2)	O-10	LV(1)	X-29	0.11	-	-	-	-
LP(2)	O-10	RY(1)	X-29	0.45	-	-	-	-
LP(2)	O-10	RY(3)	X-29	0.06	-	-	-	-
LP(3)	O-10	RY(2)	X-29	0.26	-	-	0.1	-
BD(1)	C1 – H2	LV(1)	X-29	0.11	0.14	0.08	0.11	0.09
BD(1)	C1 – H3	LV(1)	X-29	0.08	0.12	0.08	-	0.09
BD(1)	C1 – C4	LV(1)	X-29	-	-	-	0.05	-

BD(1)	O8 – C9	LV(1)	X-29	0.07	0.09	0.05	-	-
BD(1)	C9 – O10	LV(1)	X-29	0.14	-	-	-	-
BD(1)	C9 – O10	RY(3)	X-29	0.13	-	-	-	-
BD(1)	C9 – C11	LV(1)	X-29	0.39	0.31	0.14	0.09	0.05
BD(1)	C11 – H12	LV(1)	X-29	-	0.07	-	-	-
BD(1)	N16 – H18	LV(1)	X-29	-	0.05	0.05	0.06	0.05
CR(7)	*X-29*	*RY(3)*	*O-10*	-	-	*0.05*	-	-
CR(3)	*X-29*	*RY(3)*	*O-10*	-	-	-	-	*0.07*

‘X$^+$’ denotes ‘metal ions’. ‘Unit 1 to Unit 2’ charge transfer is depicted in normal texts. ‘Unit 2 to Unit 1’ charge transfer is depicted in *italic* texts. Metal ions is in ‘Unit 1’ and rest of the atoms are in ‘Unit 2’. ‘SE’ denotes ‘the stabilization gained (kcal/mol) by donation from the donor NBO to the acceptor NBO’. ‘LP’ denotes ‘lone-pair’, ‘LV’ denotes ‘lone vacant’, ‘RY’ denotes ‘Rydberg’, ‘BD’ denotes ‘bonding’, and ‘CR’ denotes ‘core’ orbitals. Entries are included in this table only when the interaction energy exceeds a default threshold of 0.05 kcal/mol.

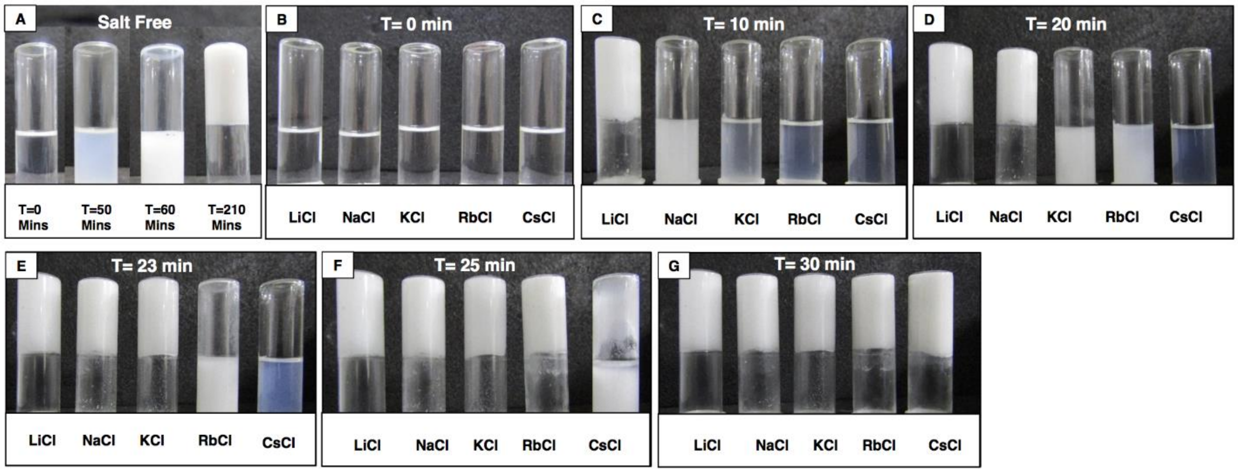


Fig. S1. A) Digital images showing the conversion of reaction mixture of BPEI/5AcI into gel in absence of any salt. B-G) Digital images illustrating the progress of gelation of same reaction mixtures in presence of various alkali metal salts including LiCl, NaCl, KCl, RbCl and CsCl. The transparent reaction mixtures with different alkali metal salts turned into polymeric gel at different times (10 min for LiCl, 20 min for NaCl, 23 min for KCl, 25 min for RbCl and 30 min for CsCl).

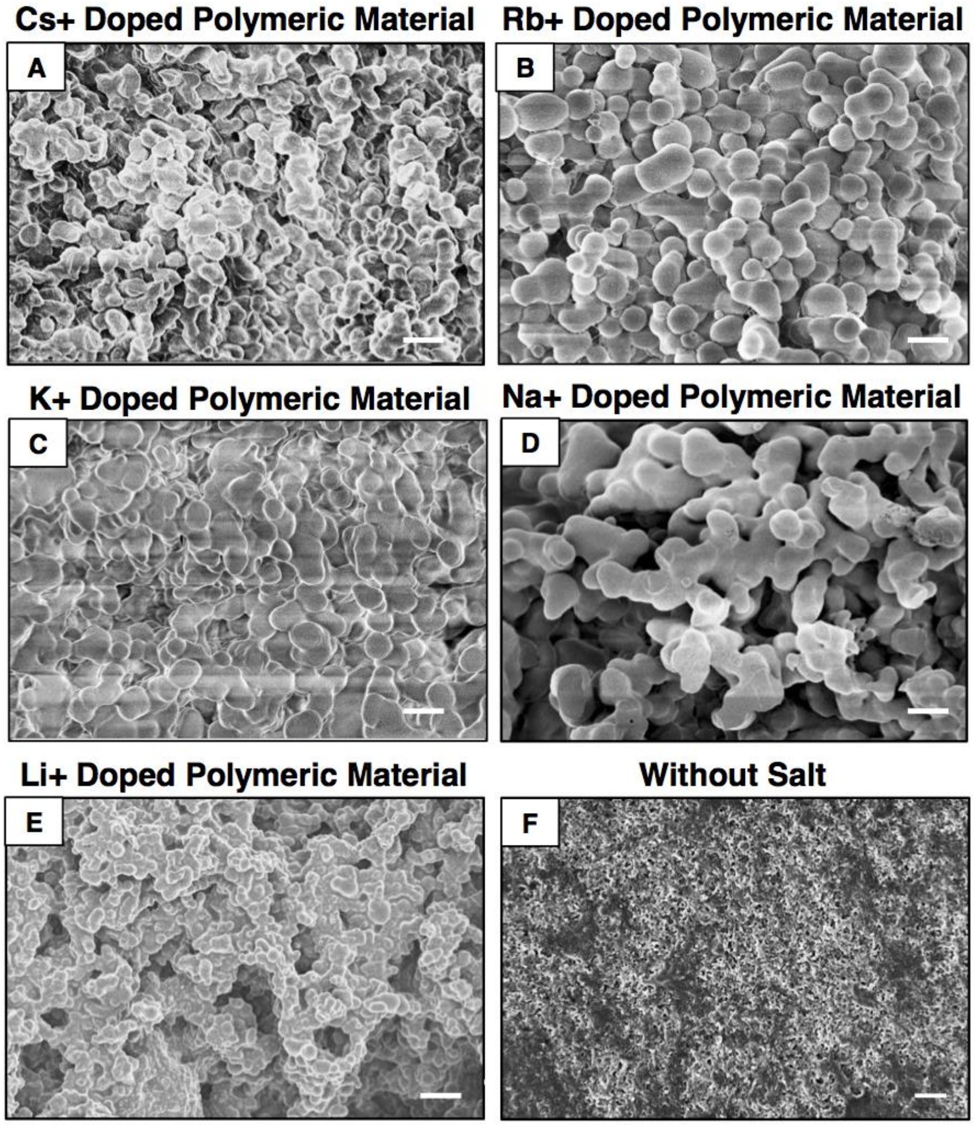


Fig. S2. (A-F) FESEM images of polymeric material that are synthesized in presence of various alkali metal salts including CsCl (A), RbCl (B), KCl (C), NaCl (D), CsCl (E) and without salt (F) respectively (Scale Bar; 1μM).

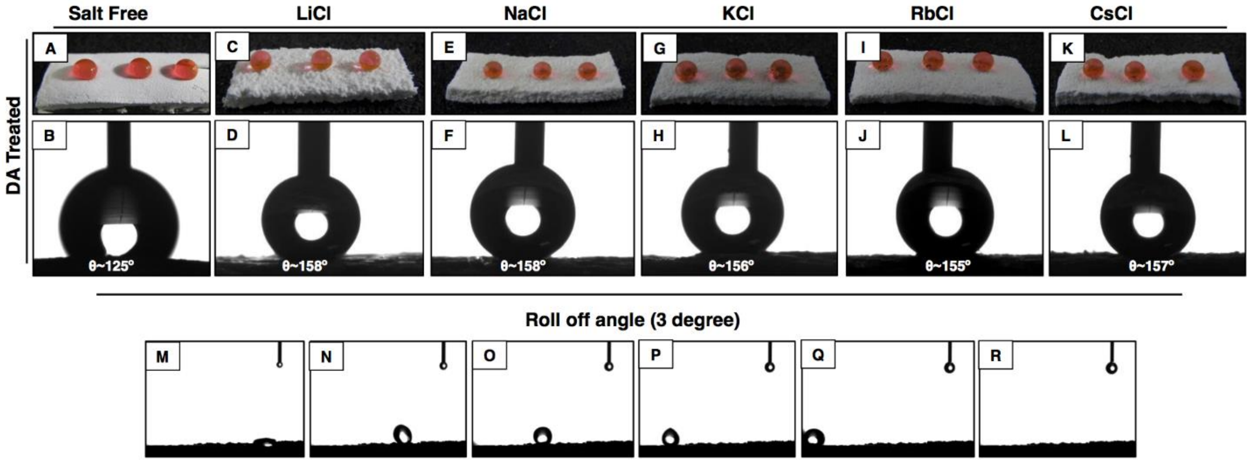


Fig. S3. (A-L) Digital images (A, C, E, G, I ,K) and contact angle images (B, D, F, H, J, L) of polymeric material without any salt (A, B) and after doping with various alkali metal salts (10 mM) including LiCl (C, D), NaCl (E, F), KCl (G, H), RbCl (I, J) and CsCl (K, L) after post modification with decylamine. M-R) Images displaying the rolling of water droplet from the surface of polymeric material after tilting at 3° angle.

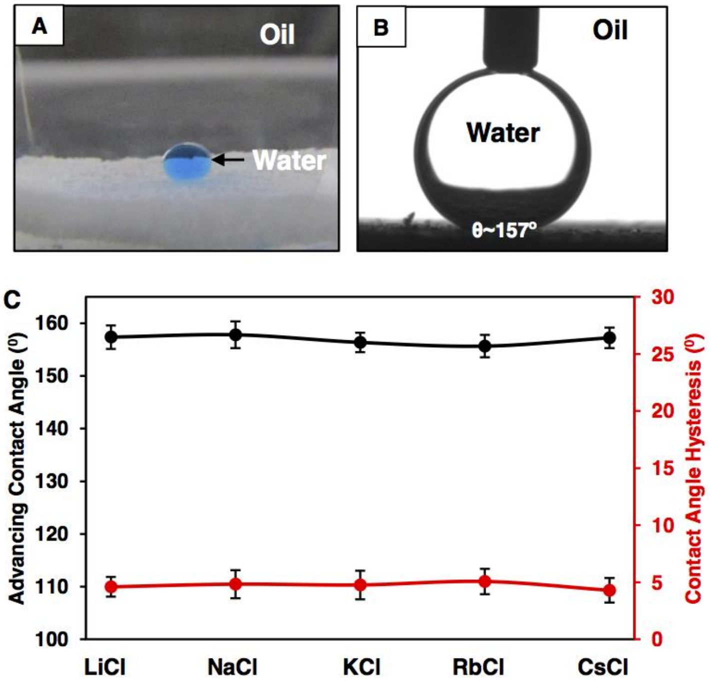


Fig. S4. A-B) Digital image (A) and water contact angle (B) of polymeric material under oil (n-hexane). C) Plot showing advancing contact angle (black) and contact angle hysteresis (red) of beaded water droplet under oil (n-hexane) on polymeric materials that are synthesized in presence of various alkali metal salts (i.e.; LiCl, NaCl. KCl. RbCl, CsCl ; concentration of each salt is10 mM) and post chemical modified with decylamine molecules.

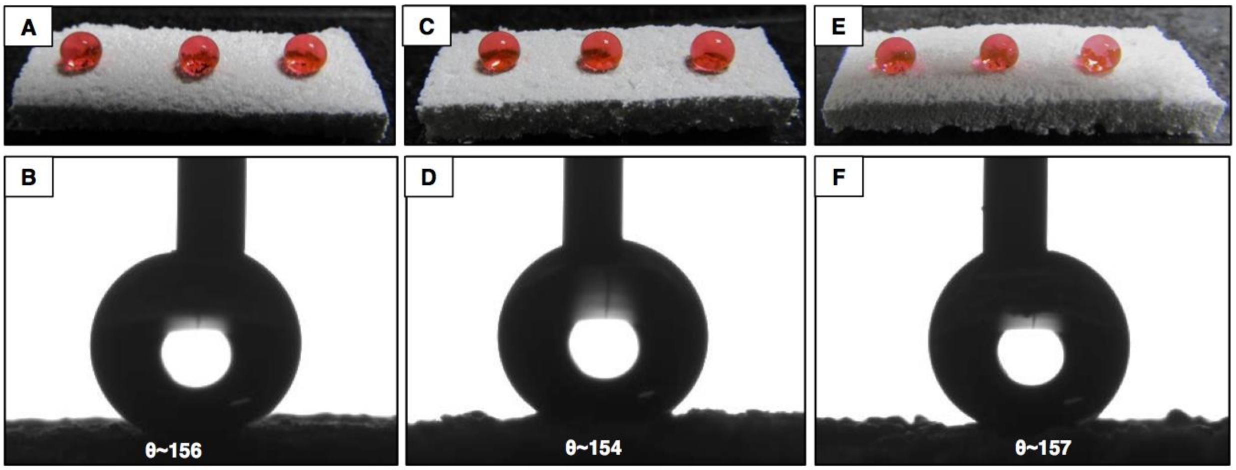


Fig. S5. A-F) Digital images (A, C, E) and contact angle images (B, D, F) of beaded water droplet on polymeric material that are developed in presence of different concentrations of LiCl including 10 mM (A, B), 20 mM (C, D), 30 mM (E, F) and post chemically modified with decylamine molecules.

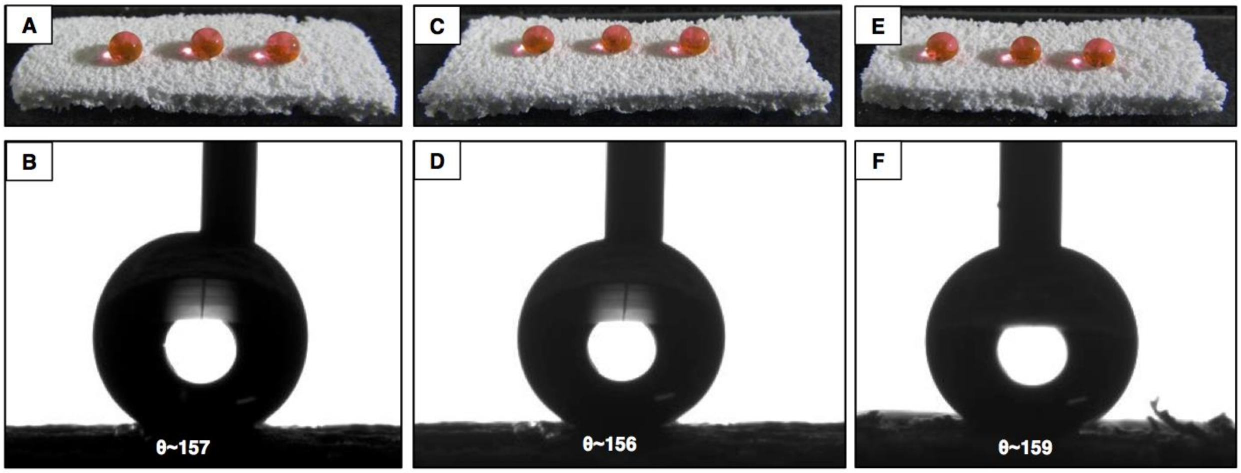


Fig. S6. A-F) Digital images (A, C, E) and contact angle images (B, D, F) of beaded water droplet on polymeric material that are developed in presence of different concentrations of NaCl including 10 mM (A, B), 20 mM (C, D), 30 mM (E, F) and post chemically modified with decylamine molecules.

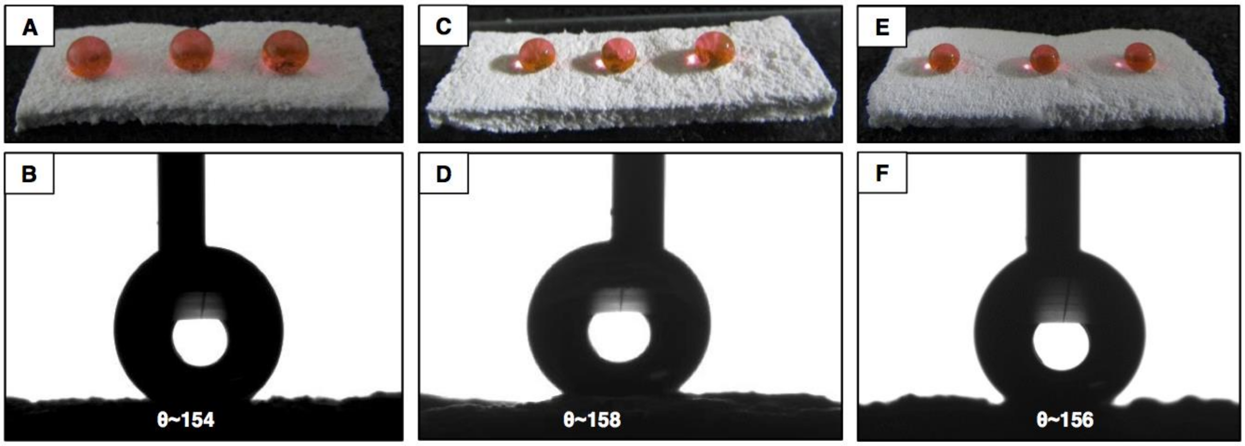


Fig. S7. A-F) Digital images (A, C, E) and contact angle images (B, D, F) of beaded water droplet on polymeric material that are developed in presence of different concentrations of KCl including 10 mM (A, B), 20 mM (C, D), 30 mM (E, F) and post chemically modified with decylamine molecules.

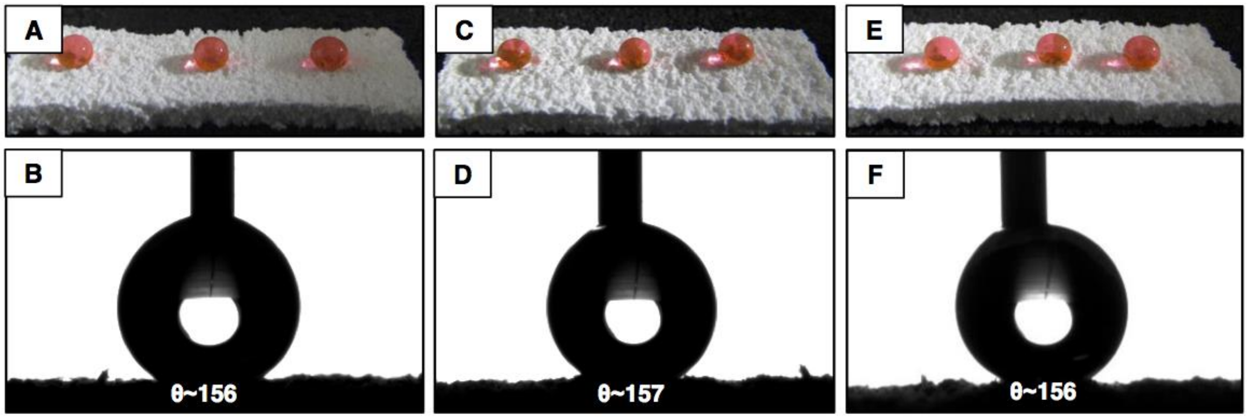


Fig. S8. A-F) Digital images (A, C, E) and contact angle images (B, D, F) of beaded water droplet on polymeric material that are developed in presence of different concentrations of RbCl including 10 mM (A, B), 20 mM (C, D), 30 mM (E, F) and post chemically modified with decylamine molecules.

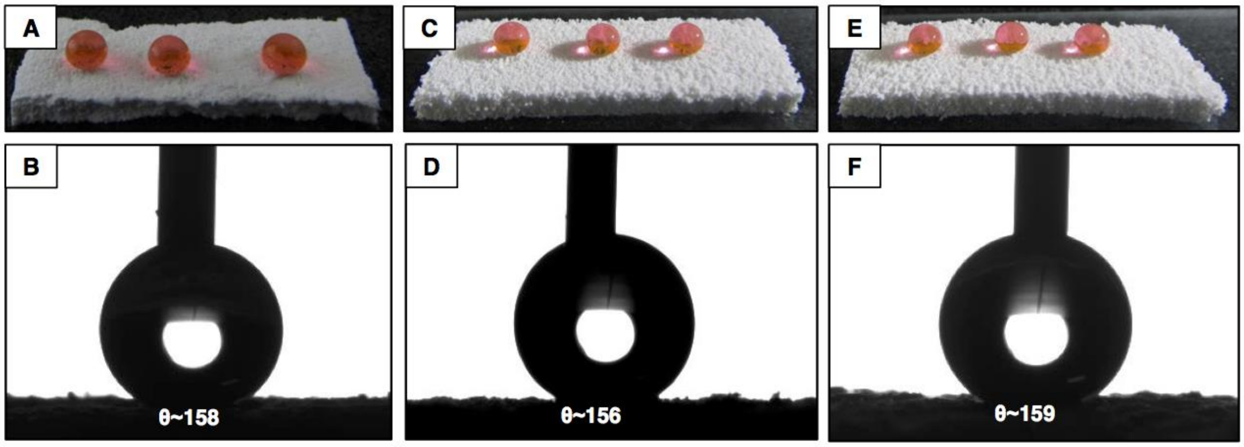


Fig. S9. A-F) Digital images (A, C, E) and contact angle images (B, D, F) of beaded water droplet on polymeric material that are developed in presence of different concentrations of CsCl including 10 mM (A, B), 20 mM (C, D), 30 mM (E, F) and post chemically modified with decylamine molecules.

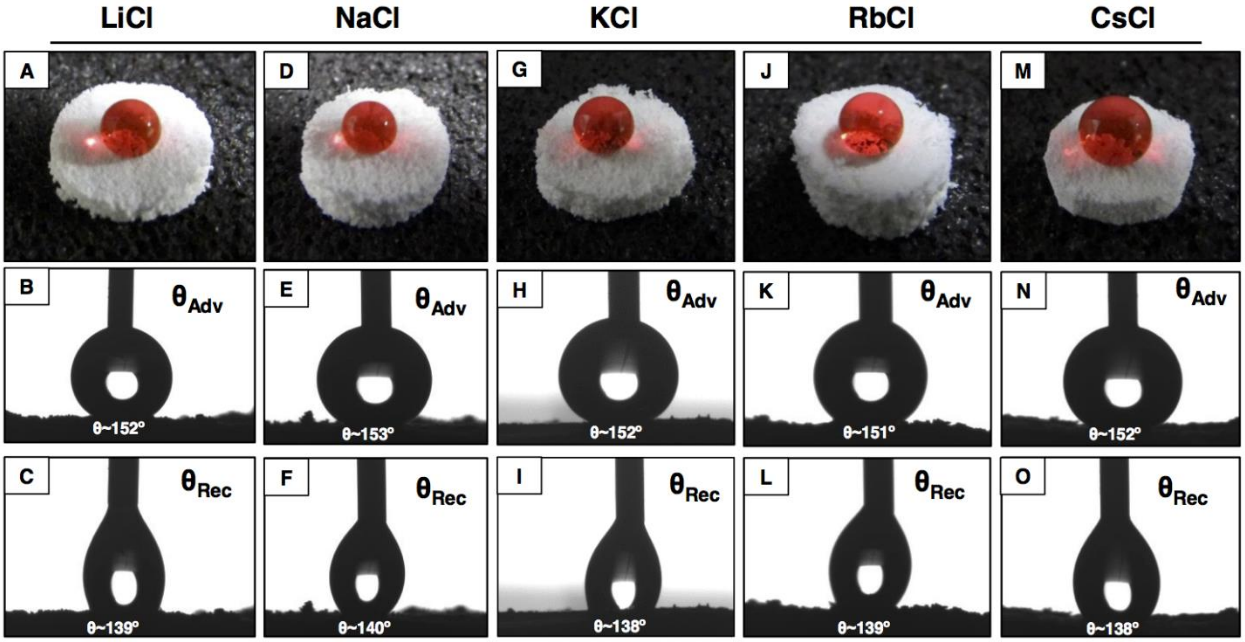


Fig. S10. A-O) Digital images (A, D, G, J, M), advancing contact angle (B, E, H, K, N) and receding contact angle (C, F, I, L, O) of beaded water droplet on polymeric materials that are synthesized in presence of various alkali metal salts including LiCl (A, B, C), NaCl (D, E, F), KCl (G, H, I), RbCl (J, K, L) and CsCl (M, N, O), after the post chemical modification of each material with octylamine molecules.

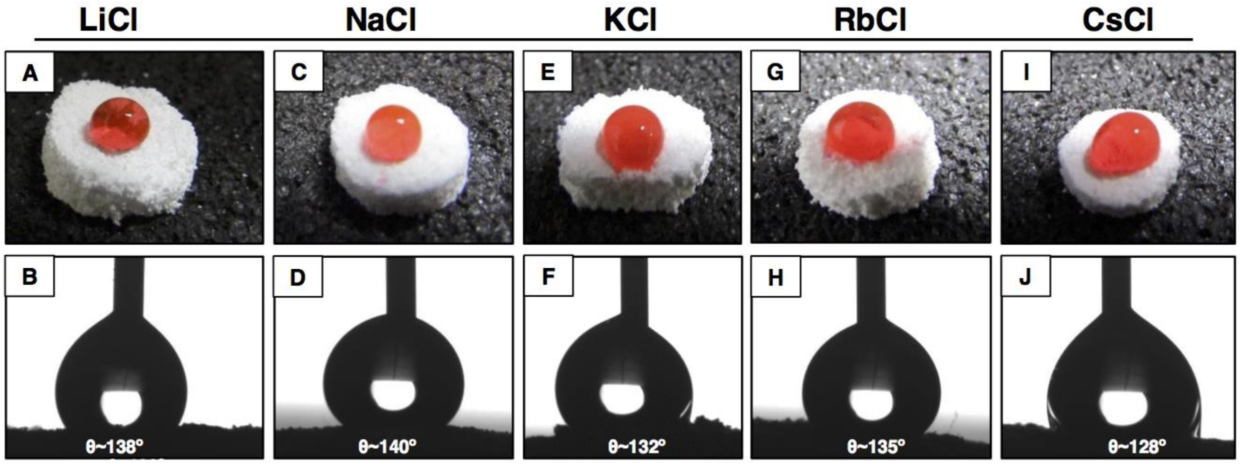


Fig. S11. A-J) Digital images (A, C, E, G, I), advancing contact angle (B, D, F, H, J) of beaded water droplet on polymeric materials that are synthesized in presence of various alkali metal salts including LiCl (A, B, C), NaCl (D, E, F), KCl (G, H, I), RbCl (J, K, L) and CsCl (M, N, O), after the post chemical modification of each material with hexylamine molecules.

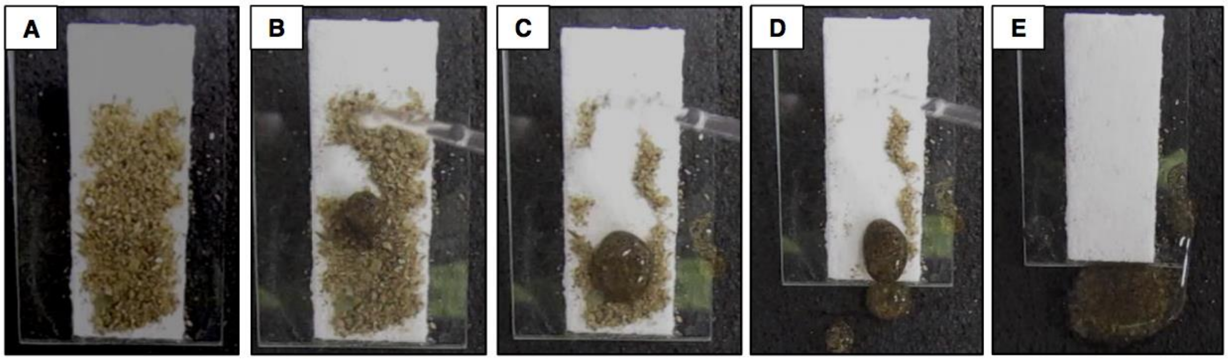


Fig. S12. A-E) Digital images depicting the self-cleaning performance of deposited dust particles on the polymeric material that prepared in the presence of LiCl (10mM) and post modified with decylamine.

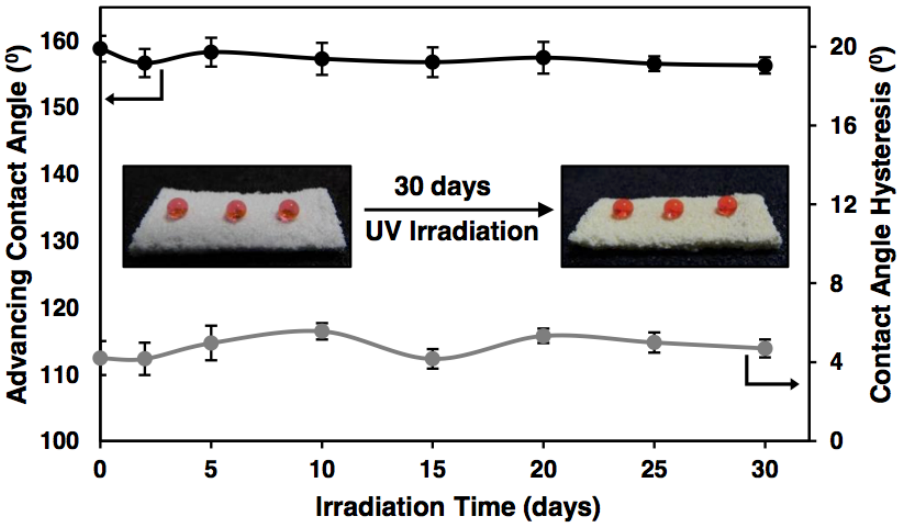


Fig. S13. The plot illustrating the change in the advancing contact angle (black) and contact angle hysteresis (grey) of beaded water droplet on the polymeric material (that is prepared in the presence of LiCl (10 mM) and post modified with decylamine), after exposing to UV radiations at short (256 nm) and longer (384nm) wavelengths for 30 days. Inset is the digital images of beaded water droplet on polymeric material before and after exposing to UV irradiation for 30 days).

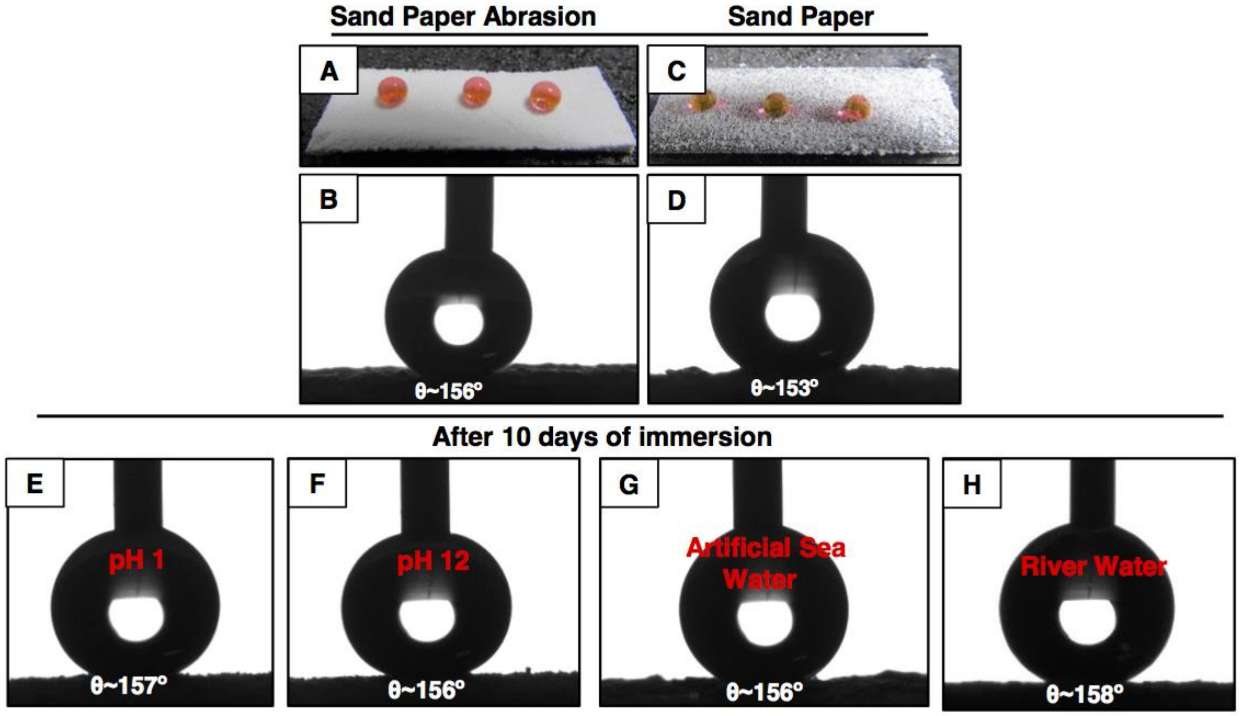


Fig. S14. A-D) Digital images (A, C) and contact angle images (B, D) of beaded water droplet on the polymeric material after performing the sand paper abrasion test (A, B), and abrasive sand paper that coated with powdery materials after the abrasion process (C, D) is capable of repelling water extremely with water contact angle above 150°. E-H) Contact angle images of beaded water droplet on polymeric material (synthesized in presence of LiCl (10 mM) and post modified with decylamine molecules) after immersion in various chemically harsh aqueous conditions—including pH 1 (E), pH 12 (F), artificial sea water (G), river (Brahmaputra, Assam India) water (H).

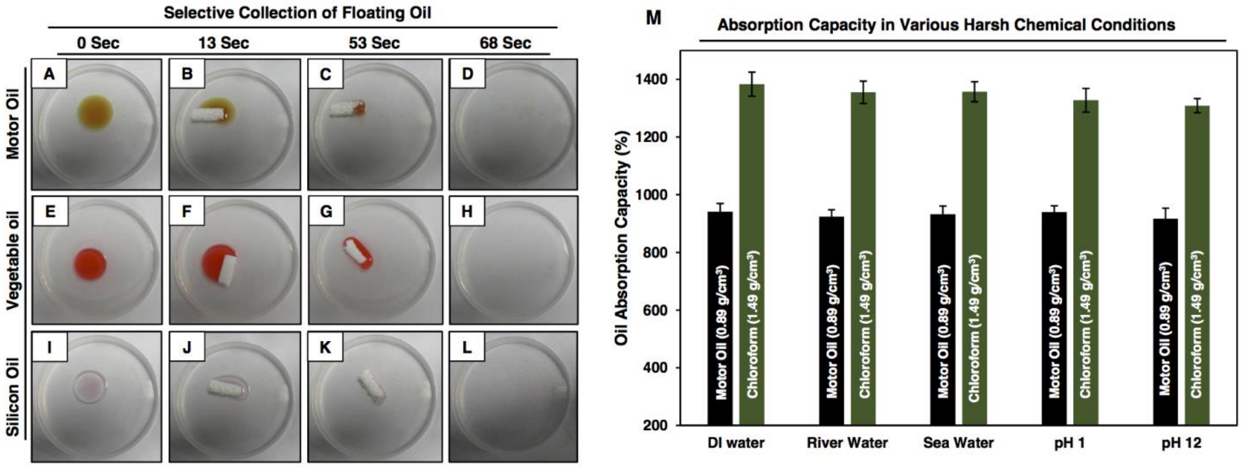


Fig. S15. A-L) Digital images illustrating the separation of floating oils (motor oil (A-D), soyabean oil (E-H), silicon oil (I-L)) droplet from the water/air interface, including using the superhydrophobic polymeric material. M) Plot accounting the selective oil absorption capacity of polymeric material that is prepared in the presence of LiCl (30 mM, post modified with decylamine) in various harsh aqueous chemical conditions including extremes of pH (pH 1 & 12), artificial sea water and river (Brahmaputra, Assam India) water for both lighter (Motor oil, black) and heavier (chloroform—model heavy oil; green) oils.

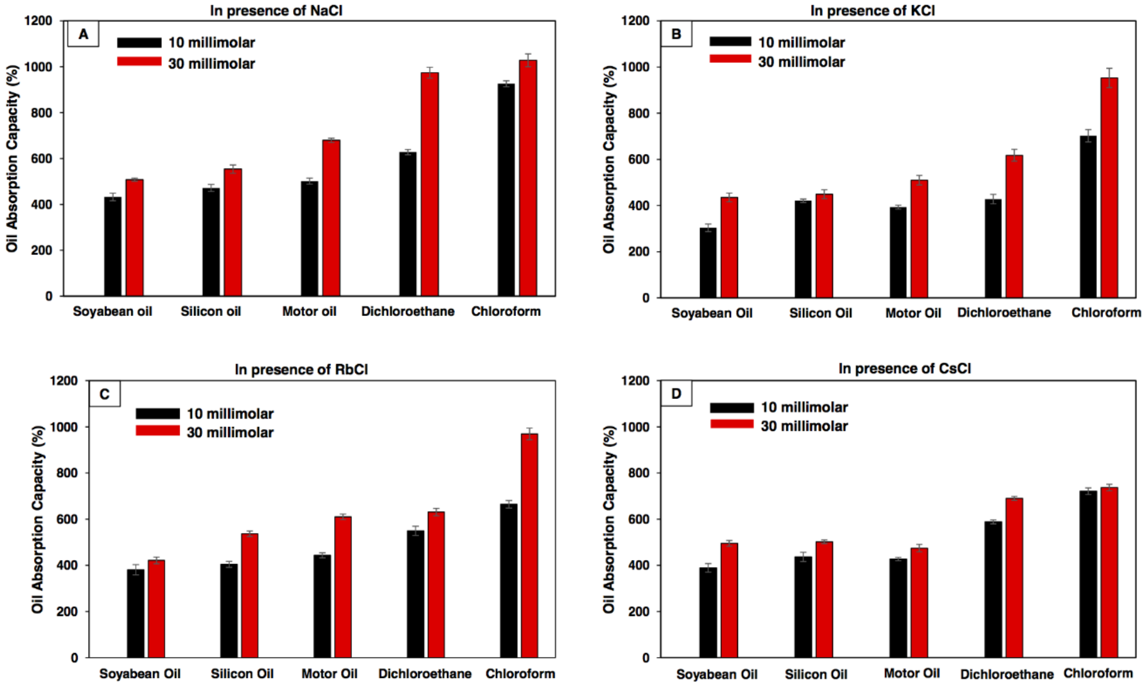


Fig. S16. A-D) Plots illustrating the selective oil-absorption capacity (both light and heavy oils) of polymeric material that are prepared in presence of various alkali metal salts including NaCl (A), KCl (B), RbCl (C), CsCl (D) at different concentrations (10mM, black; 30mM, red) of the selected salts.

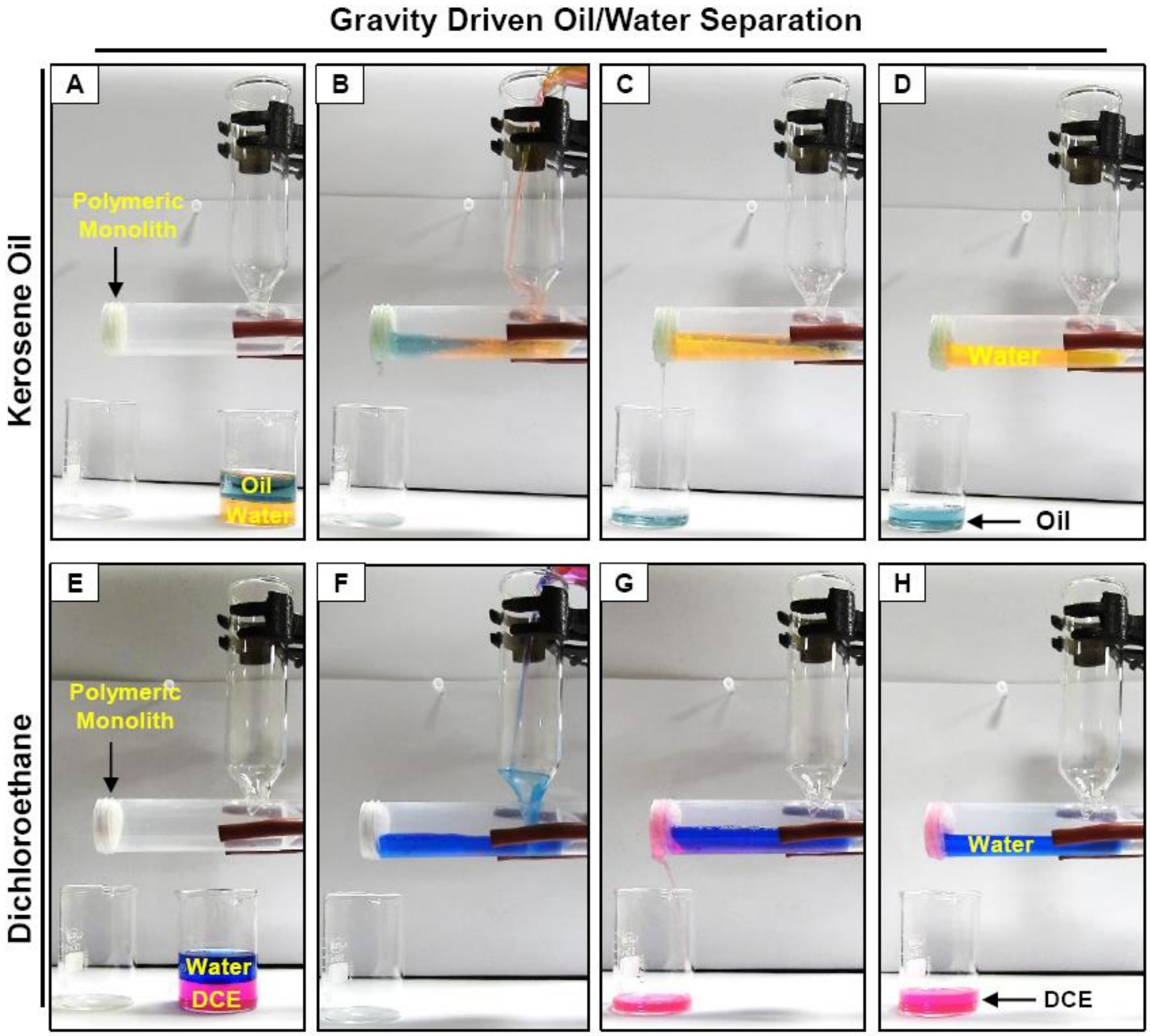


Fig. S17. A-H) Digital images showing the gravity driven separation of oil/water mixture (15 mL oil in 15 mL of water) using as synthesized polymeric material (prepared in presence of 30 mM of LiCl and post modified with decylamine), the lab-made prototype was capable of separating both light oil (kerosene; A-D) and heavy oil DCE (E-H) from respective oil water mixtures. Oil and water phases are coloured with added dyes for better visual inspections.