Electronic Supplementary Information

A Superhydrophobic Covalent Zeolitic Imidazolate Framework-Polyhedral Oligomeric Silsesquioxane Hybrid Material as a Highly Efficient and Reusable Sorbent for Organic Solvents

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Contents

Synthesis of POSS-NH_2

To a solution of isobutyl-T_7-triol (2 g, 2.53 mmol) in dichloromethane (20 mL), 3-aminopropyltrimethoxysilane (0.5 ml, 2.79 mmol) in dichloromethane (20 mL) was added under nitrogen atmosphere at RT. The reaction mixture was stirred for 48 h, then the colourless solution evaporated under vacuum to afford colourless solid (POSS-NH_2). Yield: 2.29g (90%). IR (KBr, cm^{-1}): 3372(br), 2951(s), 2871(s), 1464(m), 1365(s), 1327(w), 1228(s), 1171(m), 1087(s), 1037(m), 954(m), 841(m), 746(s), 684(w), 557(w). ^1H NMR (500 MHz, $CDCl_3$, TMS, ppm): δ = 0.59 (t, 2H, -$\mathit{CH_2}CH_2CH_2NH_2$), 0.62(d, 14H, -$CH_2$ in *i*Bu), 0.95 (dd, 42H, -CH_3), 1.53 (m, 2H, -$CH_2\mathit{CH_2}CH_2NH_2$), 1.85 (septet, 7H, -CH), 2.67 (t, 2H, -$CH_2CH_2\mathit{CH_2}NH_2$). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ = 44.9, 27.3, 25.8, 24.0, 22.6, and 9.3 (aliphatic-carbons). ^{29}Si NMR (79.30 MHz, $CDCl_3$, TMS, ppm): δ = −67.8, −67.6, −67.2. Positive ion ESI-Mass m/z = 874.20 [POSS-NH_2].

Estimation of $POSS\text{-}NH_2$ functionalized with ZIF-90 by TG analysis:

$$\frac{\text{The residual weight wt\% of ZIF-POSS (the cage-structural POSS) } 19.12\text{ wt\%}}{47.5\text{ wt\% The molecular weight fraction of the cage-structural POSS in POSS-NH}_2} = 40.25\text{ wt\%} \quad \text{Quantity of POSS-NH}_2\text{ functionalized with ZIF-90}$$

ZIF-POSS: ZIF = 59.75 wt%, ratio: 3 POSS = 40.25 wt%, ratio: 2

a) b)

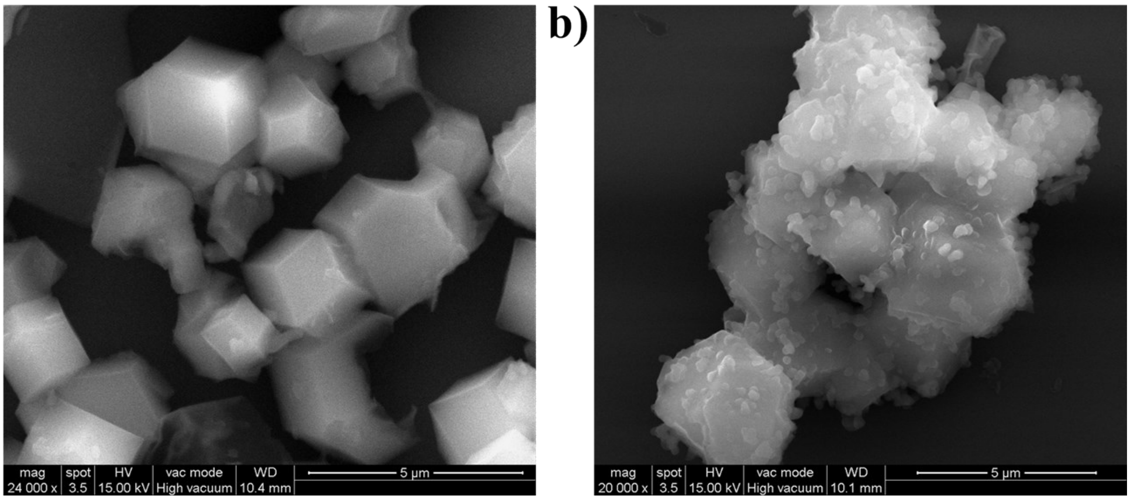

Figure S1. FE-SEM images of (a) ZIF-90; (b) ZIF-POSS.

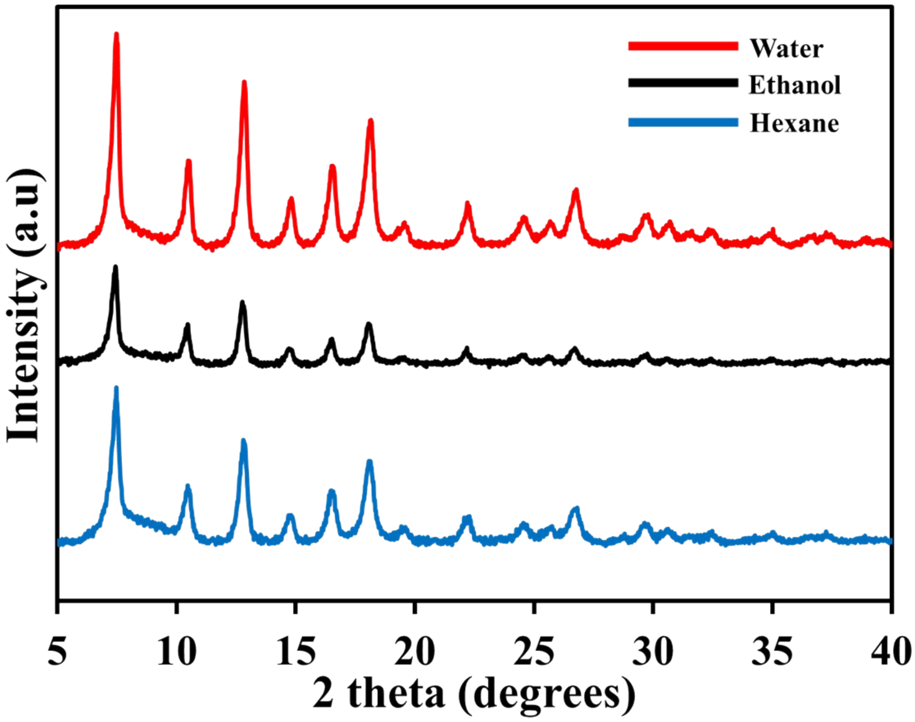

Figure S2. PXRD patterns of ZIF-POSS in boiled water, ethanol and hexane for 24 h.

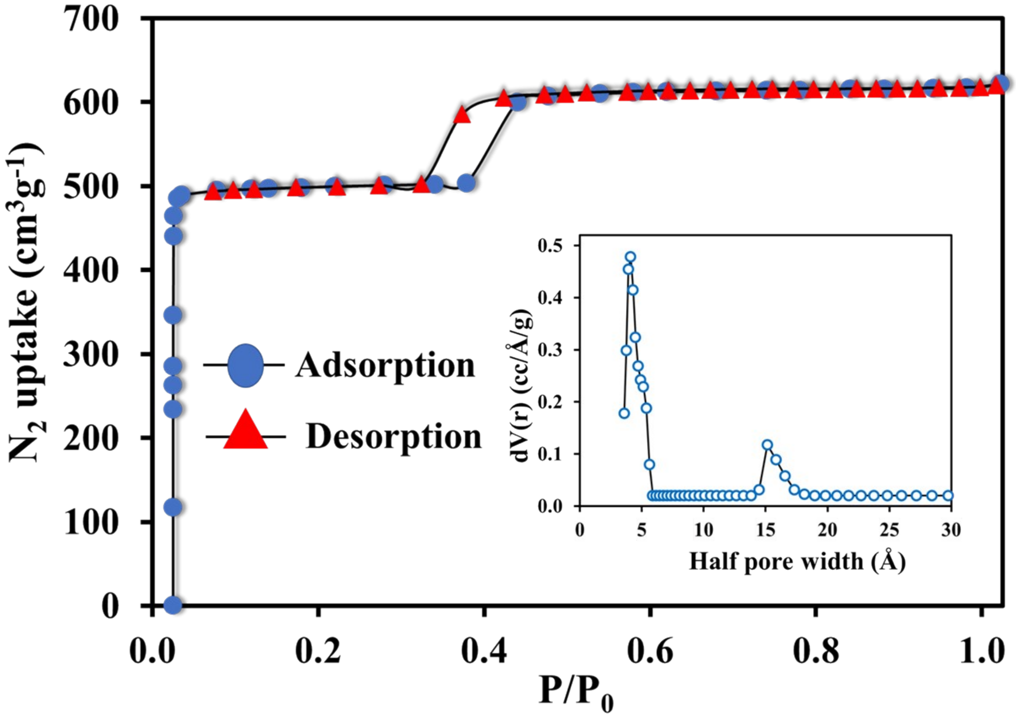

Figure S3. N_2 isotherm for ZIF-90, inset shows the pore size distribution measured at 77 K (Blue and red circles represent adsorption and desorption, respectively).

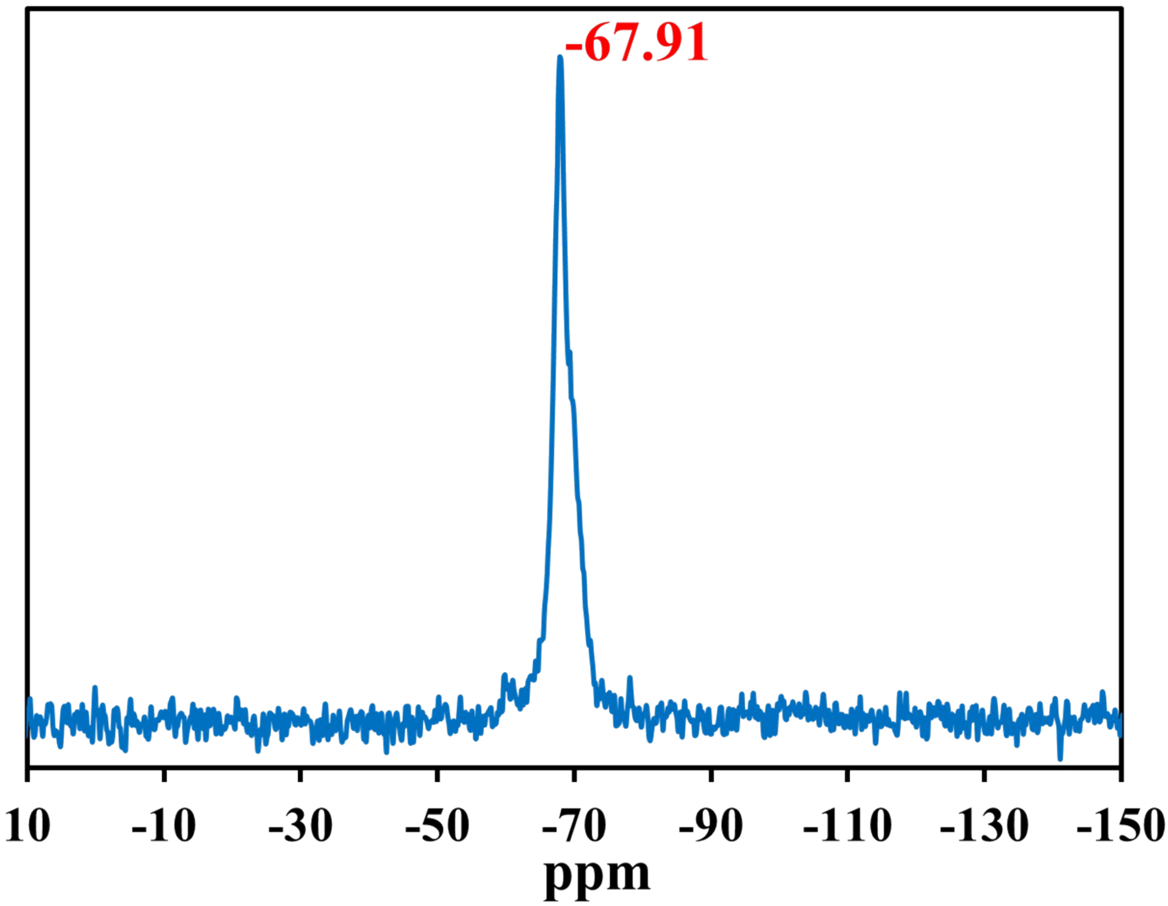

Figure S4. ^{29}Si NMR spectrum of ZIF-POSS.

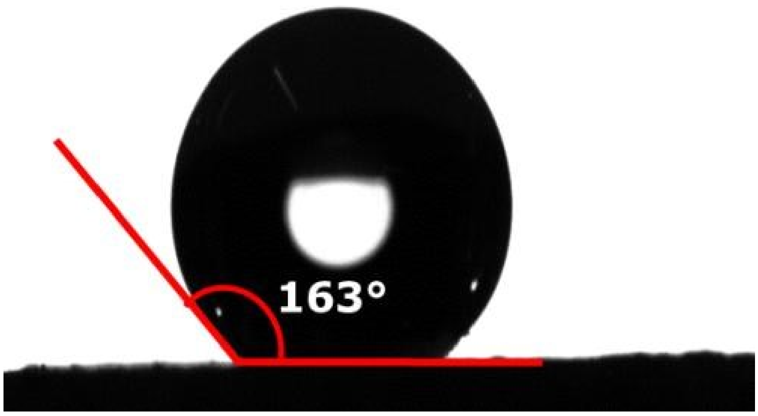

Figure S5. Photographs of water contact angle of POSS-NH_2.

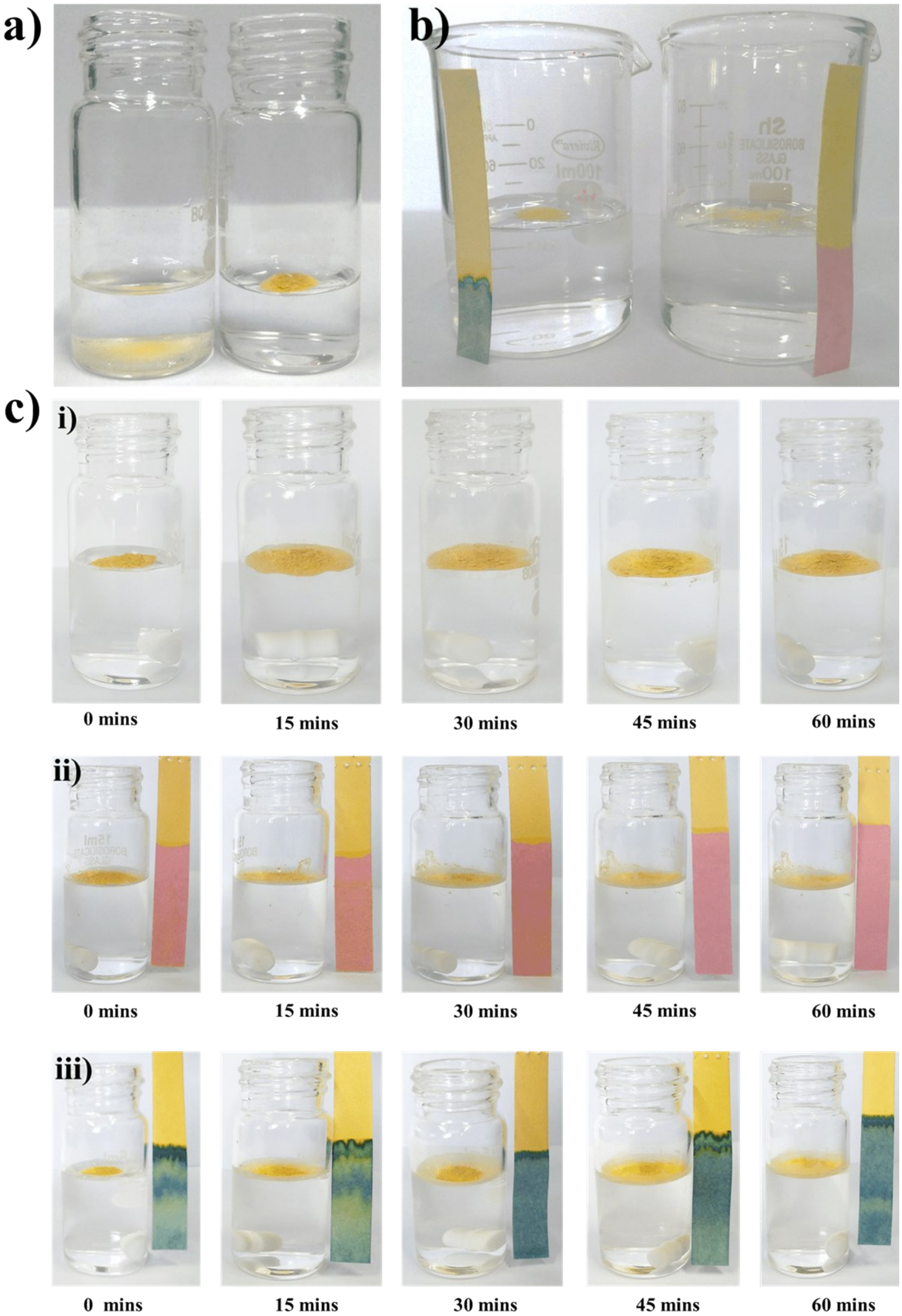

Figure S6. (a) Photographs showing the water wetting behaviour of ZIF-90 and ZIF-POSS; (b) Photographs of ZIF-POSS exposing into alkaline and acidic media. (c) ZIF-POSS in (i) water/neutral (ii)acidic and (iii) basic media under stirring (500 rpm) for different times.

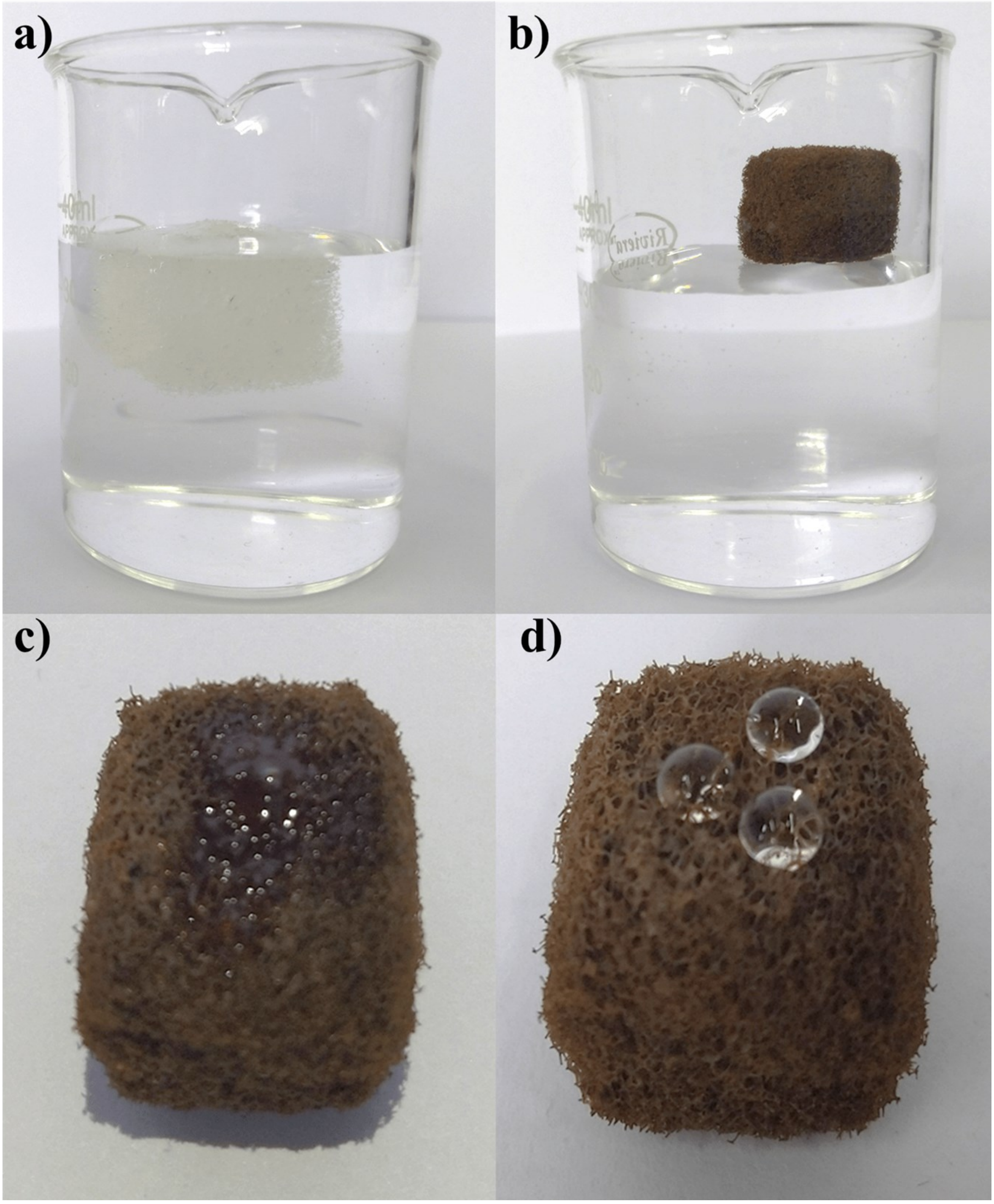

Figure S7. The picture of (a) PU sponge in water and (b) ZIF-POSS@PDA@sponge on water; (c) oil droplet on surface of ZIF-POSS@PDA@sponge; (d) water droplet on surface of ZIF-POSS@PDA@sponge.

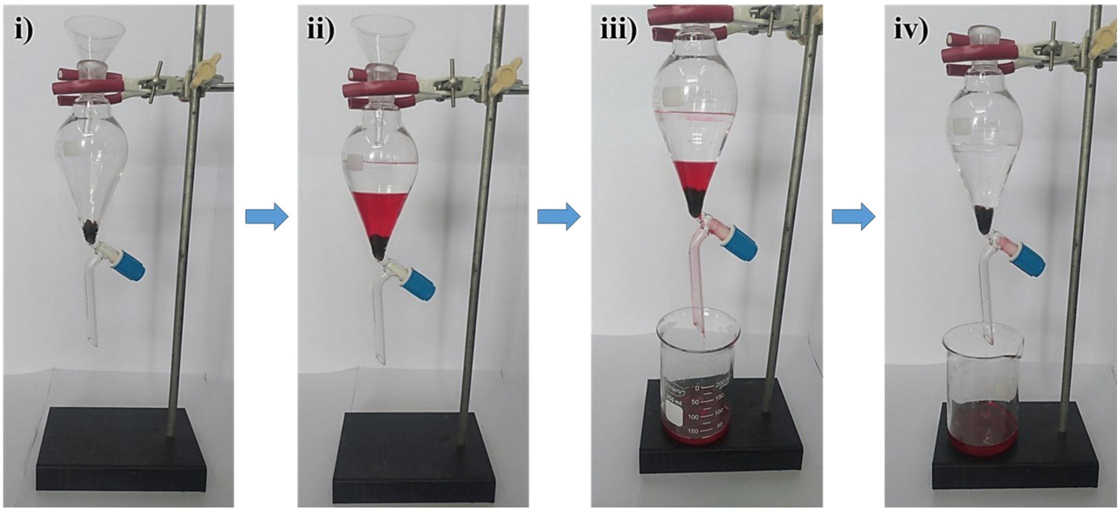

Figure S8. Photographs of chloroform-water separation using ZIF-POSS@PDA@sponge.

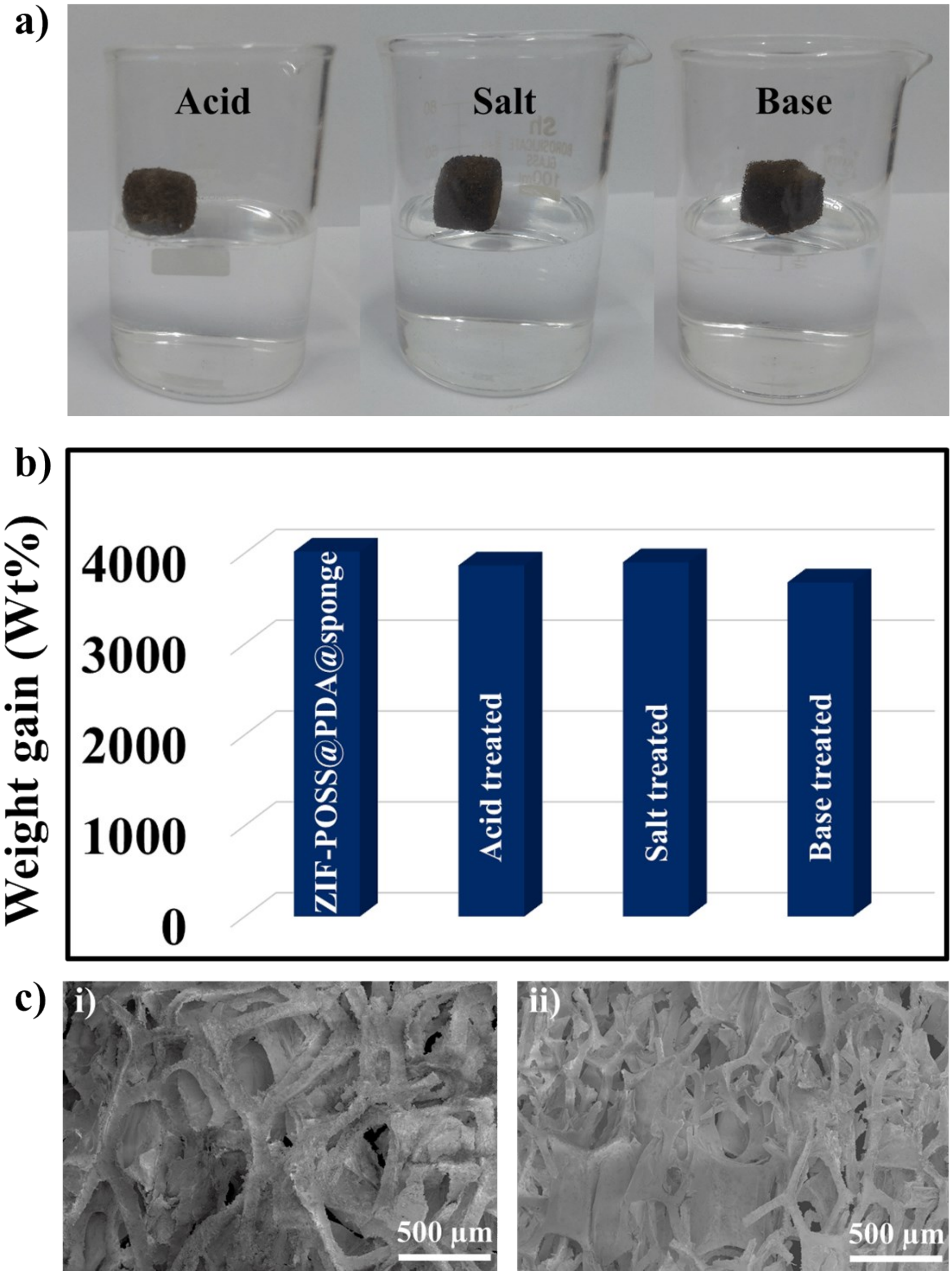

Figure S9. (a) Photographs of ZIF-POSS@PDA@sponge exposing to acidic, salt and alkaline media; (b) Testing selective ‘chloroform’ sorption for chemically treated ZIF-POSS@PDA@sponge; (c) SEM images of ZIF-POSS@PDA@sponge after exposing to acidic and alkaline media.

Table S1. Absorption capacities and separation efficiency of various POSS and MOF based materials.

S. No	Materials	Contact Angle [°]	Absorption capacities	Separation efficiency	Application	Ref
1	P(MMA-SMA-MAPOSS)	153	-	99%	Oil–water separation	1
2	TiO_2-SH-POSS@CT	157.6	-	99%	Self-cleaning and Oil–water separation	2
3	POSS-modified Luffa sponges	155	-	-	Oil absorption from water	3
4	PIM-1/POSS	155	-	99.97%	Oil−Water separation, Cleanup of Oil Soluble Contaminants	4
5	POSS-MPTMS	142	280 wt%	96%	Oil-water separation and Self-cleaning process	5
6	S-MIL-101 S-UiO-66 S-ZIF-67 S-HKUST	156±1 154±1 151±1 155±1	142-369 wt% 125-281 wt% 122-341 wt% 118-325 wt%	≥99.5%	Oil-water separation	6

7	Superhydrophobic ZIF-90	152.4	-	98%	Bio-alcohols recovered from alcohol/water mixture	7
8	F-ZIF-90@PDA@sponge	159.1	1600-4800 wt%	-	Oil-water separation	8
9	ZIF-8@ rGO@Sponge	158	1400-2900 wt%	99%	Removal of organic solvents and oils from water	9
10	MF-ZIF-8@ sponge	140	1000 - 3800 wt%	-	Oil-water separation and Catalysis in a knoevenagel reaction†	10
11	ZIF-POSS	157	540–860 wt%.	>99%	Removal of Organic Pollutants from Water	This work

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