Electronic Supplementary Information

Eco-friendly Porous Composite of Octaphenyl Polyhedral Oligomeric Silsesquioxane and HKUST-1 with Hydrophobic-Oleophilic Properties towards Sorption of Oils and Organic Solvents

Kanakarasu Dharmaraj,[a] Mohandas Sanjay Kumar,[b] Nallasamy Palanisami,[c] Muthuramalingam Prakash,[b] Pushparaj Loganathan,[a] Swaminathan Shanmugan*[a]

[a]Department of Chemistry, Faculty of Engineering and Technology, SRM Institute of Science and Technology, Kattankulathur-603 203, Chengalpattu, Tamil Nadu, India.

E-mail: shanmugs2@srmist.edu.in & shanmugan0408@gmail.com

[b]Computational Chemistry Research Laboratory (CCRL), Department of Chemistry, Faculty of Engineering and Technology, SRM Institute of Science and Technology, Kattankulathur-603 203, Chengalpattu, Tamil Nadu, India.

[c]Centre for Functional Materials, Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology, Vellore-632014, Tamil Nadu, India.

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Synthesis of Octaphenyl POSS

Octaphenyl POSS was synthesized according to the previously reported literature.[1,2] Initially, 0.3 grams of KOH were suspended in 40 ml of toluene in a dried 100 ml double-neck round-bottom flask under a nitrogen atmosphere. To the above reaction mixture, 3.6 ml of phenyltriethoxy silane was added, and the solution was refluxed at 110 ^{o}C. Subsequently, 0.5 ml of water was methodically introduced at three-hour intervals, repeating the process three times. A white precipitate formed overnight, and the reaction solution was continuously refluxed for three days. Finally, the resulting product was filtered, washed with water and methanol, and subsequently dried overnight. Yield: 2.762 grams (86 %). FT-IR (KBr, cm^{-1}): 3079(m), 3026(m), 1596(m), 1436(m), 1138(s), 1116(s), 1028(m), 994(m), 743(s), 698(s), 623(w), 606(m), 497(m). Solid state ^{29}Si NMR CP-MAS (8 kHz, TMS, PPM): -77.7. TGA: temperature range (weight loss): 100–180 ^{o}C (7.7%), 360–850 ^{o}C (45.6%).

Octaphenyl POSS is insoluble in most the solvents but very slightly soluble in dichloromethane under hot condition.

Synthesis of HKUST-1

HKUST-1 was synthesized according to previously reported literature.[3] Briefly, 1.22 grams of $Cu(NO_3)_2 \cdot 3H_2O$ and 0.58 grams of 1,3,5-benzene tricarboxylic acid were dissolved in 5 grams of DMSO. This reaction solution was slowly added into the methanol solution and stirred continuously for 24 hours; the resulting product was obtained by centrifugation and washed with the excess amount of methanol three times, dried at 60 ^{O}C for overnight. Yield: 0.140 grams (45%). FT-IR (KBr, cm^{-1}): 3490(b), 1647(s), 1588(w), 1452(m), 1375(s), 1112(m), 936(w), 758(m), 729(s), 490(m). TGA: temperature range (weight loss): 30–250 ^{o}C (35.1%), 265–420 ^{o}C (30.1%) and 420–830 ^{o}C (22.8 %).

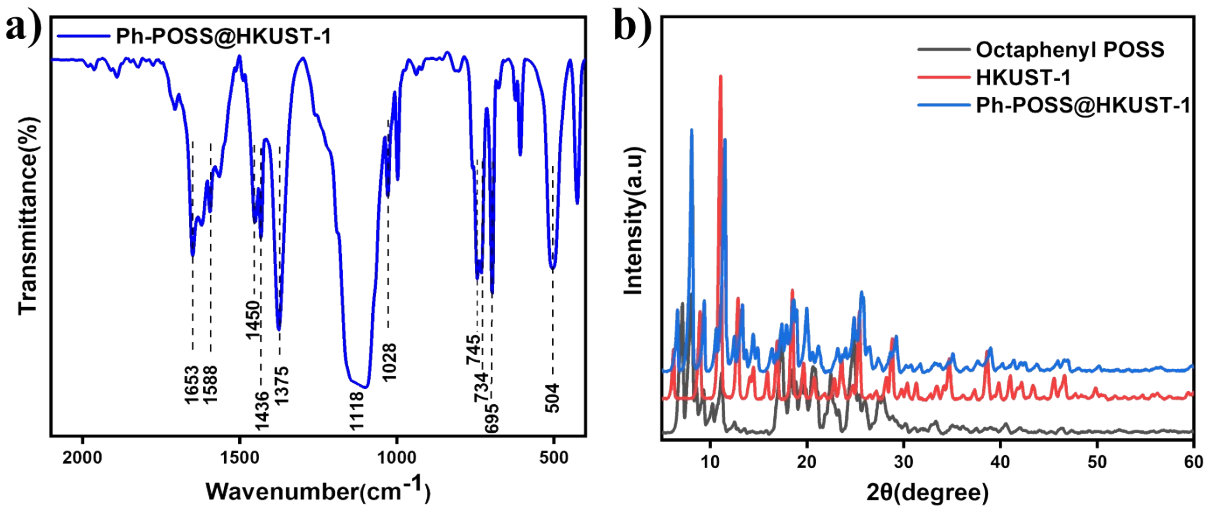

Fig. S1 (a) FT-IR spectrum of Ph-POSS@HKUST-1 (from 400 to 2100 cm^{-1}); (b) Overlapped PXRD patterns of Octaphenyl POSS, HKUST-1, and Ph-POSS@HKUST-1.

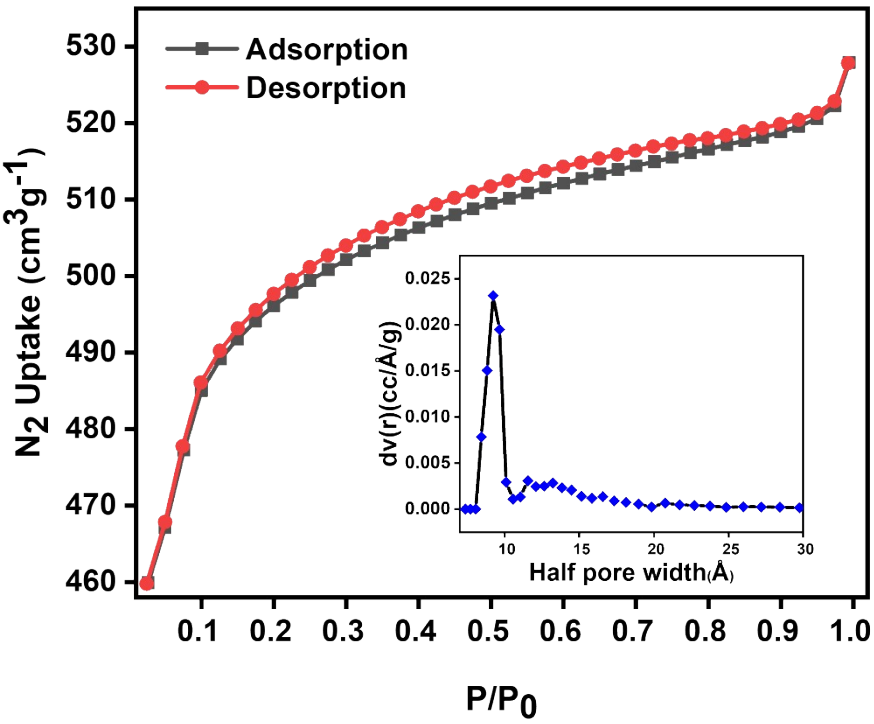

Fig. S2 N_2 isotherm for HKUST-1, inset shows pore size distribution measured at 77 K (Black and red circles represent adsorption and desorption respectively).

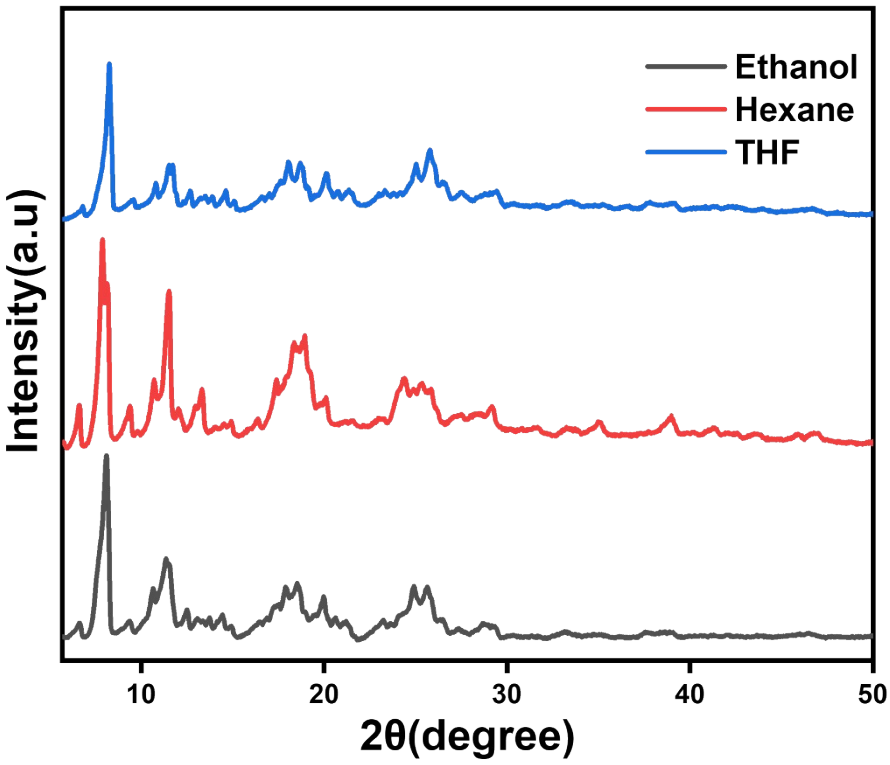

Fig. S3 Chemical stability PXRD spectra of Ph-POSS@HKUST-1 with different solvents (THF, Hexane and Ethanol).

Estimation of octaphenyl POSS composited with HKUST-1

The residual weight % of Ph-POSS@HKUST-1

(the cage structural of POSS)

$$\frac{15.2}{40.2} = 37.81\text{wt \%}$$

Quantity of Octaphenyl POSS composited with HKUST-1

The molecular weight fraction of the cage structural POSS in Octaphenyl POSS

Ph-POSS@HKUST-1:

Octaphenyl POSS = 37.81 wt%, ratio:2 HKUST-1 = 62.19 wt%, ratio: 3

Compared with the thermal decomposition behaviors of Ph-POSS and HKUST-1, Ph-POSS@HKUST-1 exhibited a significantly higher weight loss of 85 wt%. Furthermore, the amount of Ph-POSS on the HKUST-1 was estimated to be around 37.81 wt%. This estimation was performed based on the residual 15.2 wt% of the POSS cage and the molecular weight fraction of the POSS cage (40.2 wt%) in Ph-POSS, which closely matched the content of Ph-POSS in Ph-POSS@HKUST-1 during the synthesis process. The results demonstrated that incorporation of Ph-POSS to HKUST-1 in 2:3 ratio successfully leads to the formation of the Ph-POSS@HKUST-1 composite material.

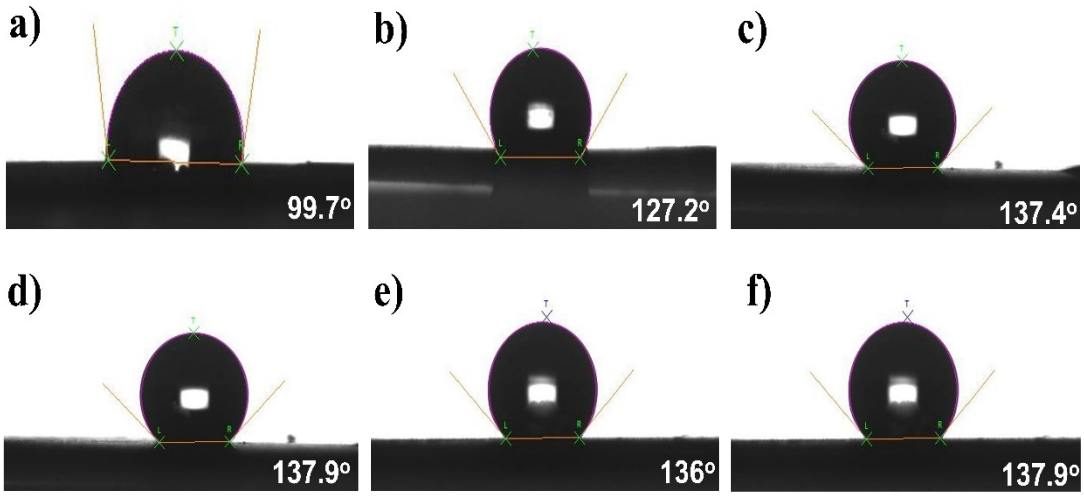

Fig. S4 Photographs show the water-wetting behavior at different (a) 0.25, (b) 0.5, (c) 0.75, (d) 1.0 (e) 1.5 and (f) 2.0 equivalents Ph-POSS loading in HKUST-1 for the synthesis of Ph-POSS@HKUST-1.

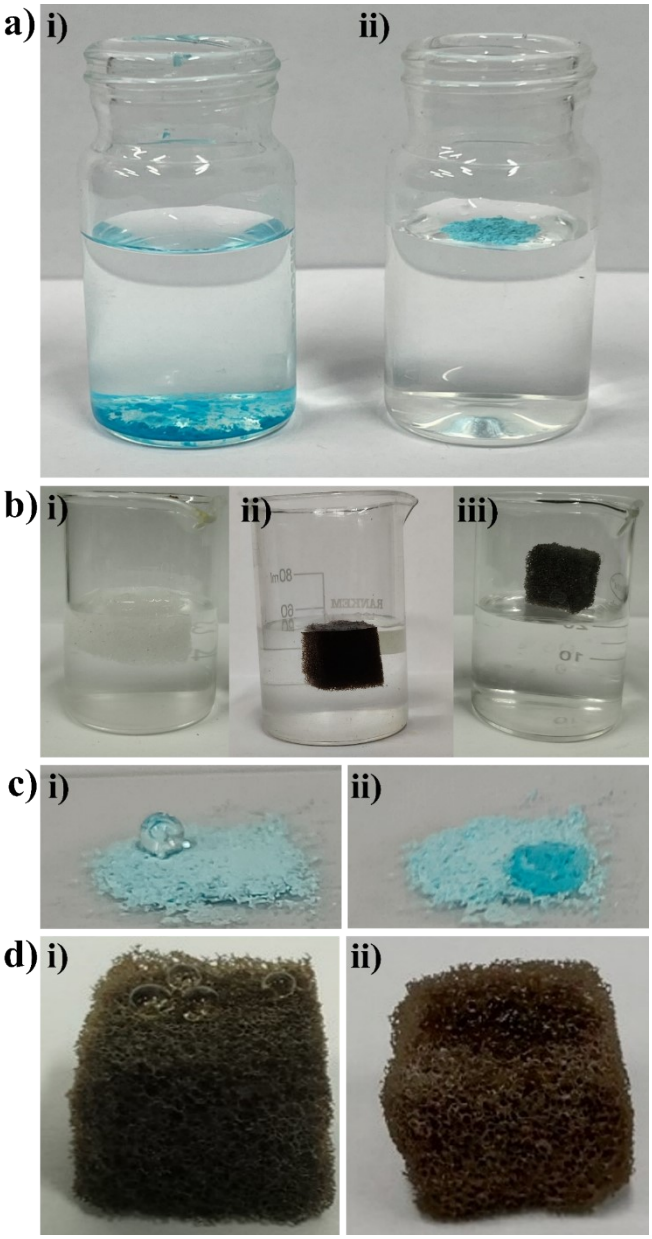

Fig. S5 Photographic images of (a) water wetting behaviour of (i) HKUST-1 (ii) Ph-POSS@HKUST-1; (b) water wetting behaviour of (i) PU sponge (ii) PDA@sponge and (iii) Ph-POSS@HKUST-1@PDA@Sponge; (c) (i) water droplet on the surface of Ph-POSS@HKUST-1, (ii) oil droplet on the surface of Ph-POSS@HKUST-1; (d) (i) water droplets on the surface of Ph-POSS@HKUST-1@PDA@Sponge, (ii) oil droplets on the surface of Ph-POSS@HKUST-1@PDA@Sponge.

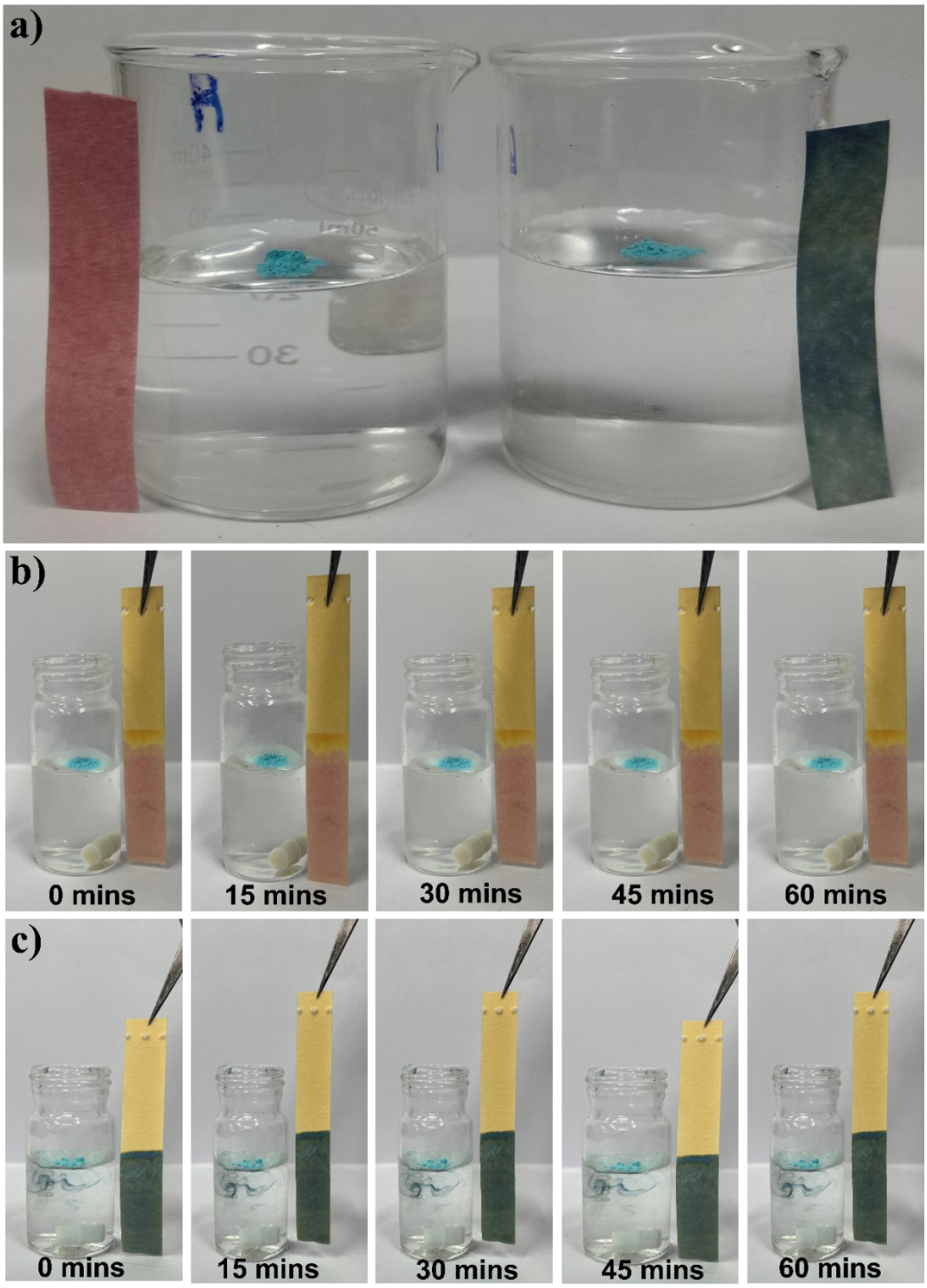

Fig S6 Photographic images of (a) Stability checkup for Ph-POSS@HKUST-1 under acid and alkaline medium; (b) Stability checkup for Ph-POSS@HKUST-1 under acidic condition with stirring at different times (500 rpm); (c) Stability checkup for Ph-POSS@HKUST-1 under alkaline condition with stirring at different times (500 rpm)

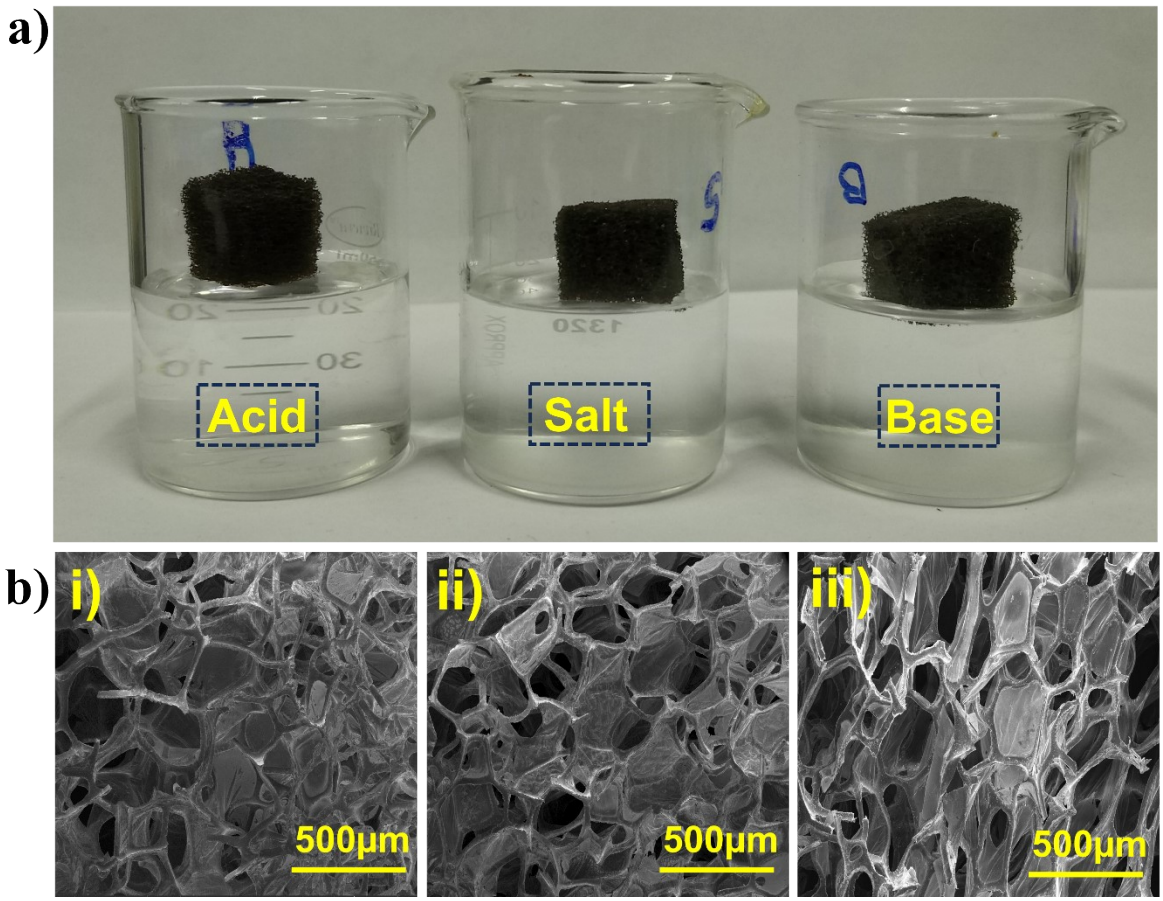

Fig. S7 (a) The photographs of Ph-POSS@HKUST-1@PDA@Sponge exposed to acid, salt, and alkaline conditions; (b) HR-SEM images of Ph-POSS@HKUST-1@PDA@Sponge after being treated with (i) acid, (ii) alkaline and (iii) salt medium.

References

1. K. Olsson and C. Gronwall, *Ark. Kemi.*, 1961, **17**, 529–540.
2. K. Song, Y. Jiang and Z. Zou, *ChemistrySelect*, 2020, **5**, 11438–11445.
3. J. L. Zhuang, D. Ceglarek, S. Pethuraj and A. Terfort, *Adv. Funct. Mater.*, 2011, **21**, 1442–1447.