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Electronic Supplementary Information (ESI)

An ultra-absorbent alkyne-rich porous covalent polycalix[4]arene for water purification

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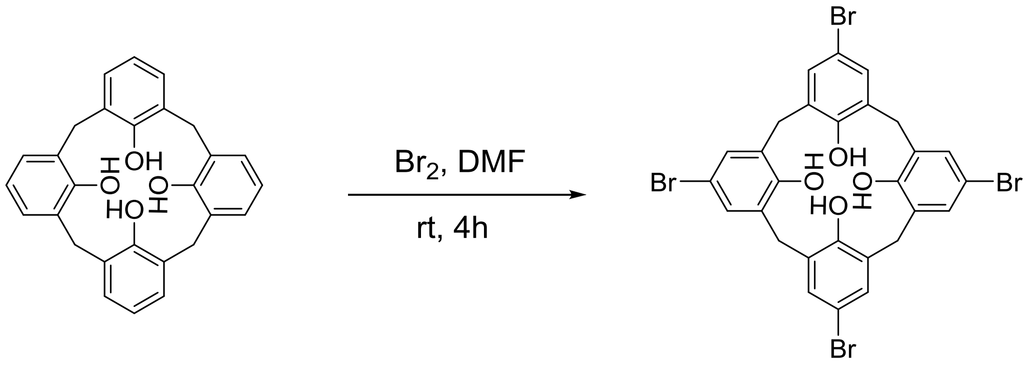
General. All the chemicals and solvents were purchased from Sigma-Aldrich and used without further purification. Deionized water was used from Millipore Gradient Milli-Q water purification system. Routine nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on a Bruker Avance spectrometer, with working frequencies of 500 MHz for ^{1}H, and 125.7 MHz for ^{13}C nuclei, respectively. All chemical shifts are reported in ppm relative to the signals corresponding to the residual non-deuterated solvent (DMSO-d_6: $\delta = 2.50$ ppm).

Materials characterization. FTIR studies were carried out on Agilent 670-IR spectrometer. TGA experiments were performed on TA SDT Q600. SEM images were obtained from FEI Quanta 450FEG. TEM images were obtained from FEI-Titan 300. Solid-state cross-polarization magic angle spinning (CP/MAS) ^{13}C NMR spectra of the polymer were recorded on a Bruker Avance 500 Wide Bore (500MHz) NMR spectrometer at ambient temperature with a magic angle spinning rate of 18.0 kHz. UV-Vis studies were carried out on Cary 5000 UV-Vis-NIR spectrophotometer. All UV-Vis spectra were recorded at room temperature using a quartz cell with 10 mm or 1 mm path length over the range 200–800 nm and corrected against an appropriate background spectrum. Surface area measurements were conducted on a Micromeritics 3Flex gas sorption analyzer. Samples (30–80 mg) were degassed at 85 °C for 24 h and then backfilled with N_2. Adsorption isotherms were generated by incremental exposure to ultrahigh-purity nitrogen up to 1 atm in a liquid nitrogen bath, and surface parameters were determined using BET adsorption models included in the instrument software (Micromeritics ASAP 2020 V4.00). The contact angles were measured using dataPhysics OCA 15EC Contact Angle (sessile drop, manual fitting) instrument.

Synthesis of 5,11,17,23-Tetrabromo-25,26,27,28-tetrahydroxycalix[4]arene.



Bromine (0.4 mL, 7.84 mol) in DMF (5 mL) was added dropwise with stirring to a solution of calix[4]arene (0.5 g, 1.18 mmol) in DMF (20 mL). The solution was stirred for 4 h. A precipitate began to form after about 0.5 h. After the 4 h of reaction, methanol (20 mL) was added, and the mixture was left to stir for an additional 0.5 h. The precipitate was filtered off and washed with methanol to yield the brominated product (0.75 g, 87%) as a white solid. ^{1}H NMR ([D6]DMSO, 25 ˚C, 500 MHz): δ = 7.34 (s, 8H, ArH), 3.81 ppm (br s, 8H, $ArCH_2Ar$). ^{13}C NMR ([D6]DMSO, 25 ˚C, 125.7 MHz): δ_c = 151.8, 131.98, 131.08, 110.89, 30.94.

Synthesis of polymer. A solution of 5,11,17,23-Tetrabromo-25,26,27,28-tetrahydroxycalix[4]arene (0.300 g, 0.408 mmol), bis(triphenylphosphine)palladium(II) chloride (0.086 g, 0.122 mmol), and copper(I) iodide (0.086 g, 0.201 mmol) in anhydrous tetrahydrofuran (30 mL) were placed in a 100 mL two-neck round-bottom flask equipped with a condenser. Diisopropylamine (1.6 mL, 1.63 mmol) and 1,4-diethynylbenzene (0.102 g, 0.816 mmol) were loaded into a separate 50 mL flask. Both solutions were sparged with N_2 for at least 15 min. The diethynylbenzene solution was then added dropwise over 5 min to the calixarene solution with stirring to afford a dark brown reaction mixture after 5 min. The reaction was heated at 65 °C under N_2 for 60 h. After cooling to room temperature, the solid product was centrifuged and washed with excess (cold and hot) tetrahydrofuran, chloroform, acetone, and (cold and hot) water to remove any unreacted monomers and metal catalyst residues. The final products were dried under a vacuum for 16 h at 60 ^{0}C to give **CalP** as a brown powder in 60 mol% yield versus the bromo-precursor.

Oil and organic solvent removal. Absorption of the following neat organic solvents and oils by **CalP** was measured: ethanol, toluene, tetraethylene glycol, used engine oil, and commercial crude oil (ATSM D5307). Dry, porous **CalP** was fully submerged in each solvent or oil for six hours to ensure complete saturation. Saturated **CalP** was removed and weighed quickly to avoid evaporation of the organic liquid. Absorption capacity values, W (wt/wt) %, were calculated by subtracting the mass of the dry porous **CalP** sample from the mass of the corresponding saturated polymer. The absorption capacity of activated carbon was tested with the same solvents and oils by following the same procedure.

Toxic dye removal. Solutions of Congo red, methylene blue and rhodamine B were prepared by dissolving each dye in deionized water. In a typical absorption test, 5 mg of **CalP** was added to 10 ml of dye solution (0.5 mM) with stirring. To monitor the absorption process, UV–Vis absorption spectra were recorded at the absorption maximum of the corresponding dye at different time intervals. The adsorption isotherms were obtained by varying the initial concentration of the dyes. The adsorption isotherms were fitted (correlation coefficients, $R^2>0.98$) by using the Langmuir adsorption model.[1]

$$Q_e = Q_m b C_e/(1+bC_e) \qquad (1)$$

where Q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium, C_e (mg l^{-1}) is the equilibrium solute concentration, Q_m is the maximum adsorption capacity corresponding to complete monolayer coverage, and b is the equilibrium constant (l mg^{-1}).

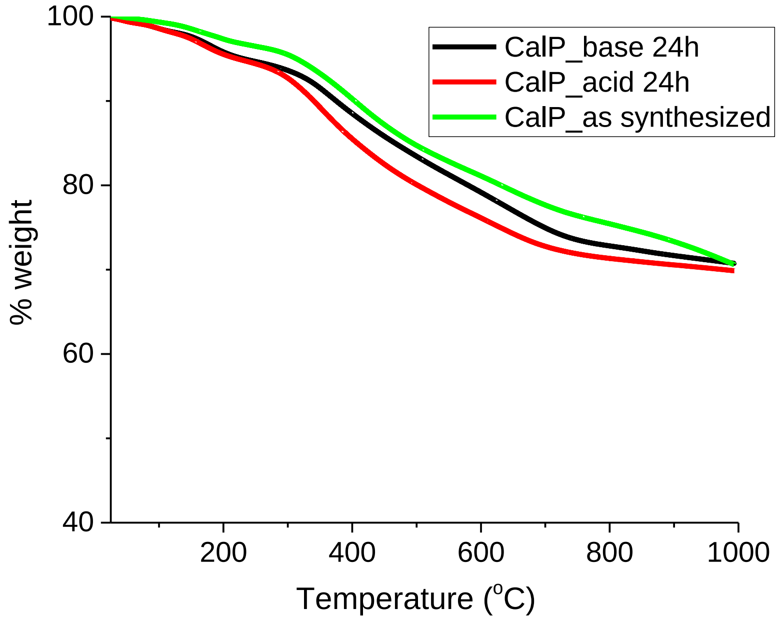


Figure S1. TGA plots for freshly synthesized **CalP** (green) and **CalP** after treatment with 1 M HNO_3 solution (red) or 1 N NaOH solution (black).

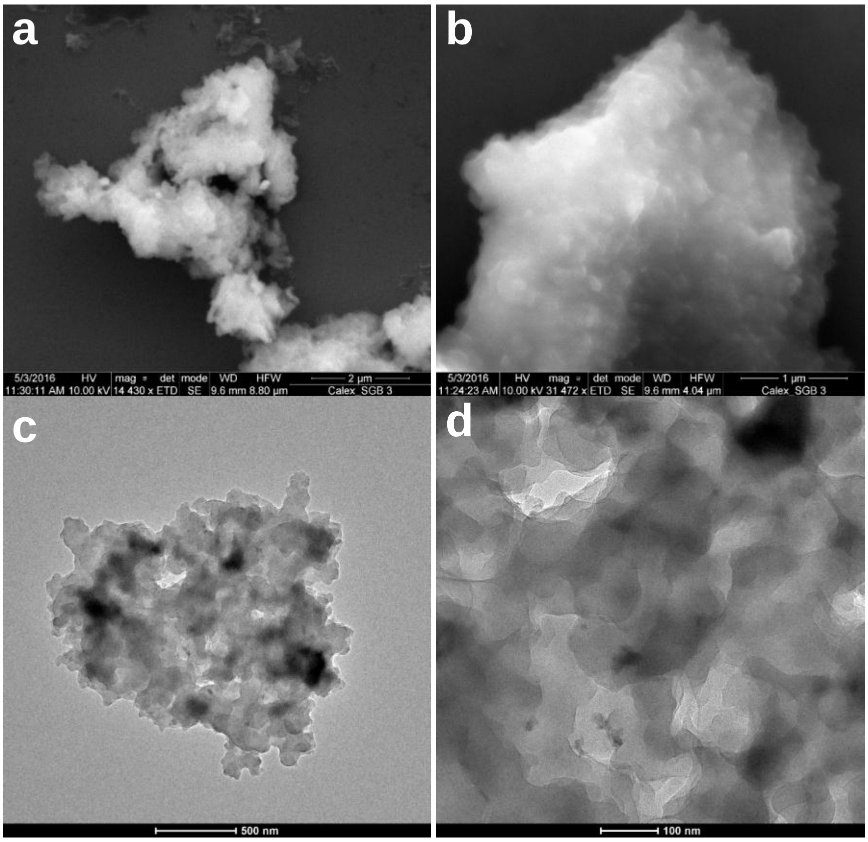


Figure S2. (**a**) Low-magnification SEM image; scale bar = 2 µm. (**b**) Magnified SEM image showing hints of porous structure; scale bar = 1 µm. (**c**, **d**) High-resolution TEM image hints the presence of pores in the polymer; scale bar = 500 and 100 nm, respectively.

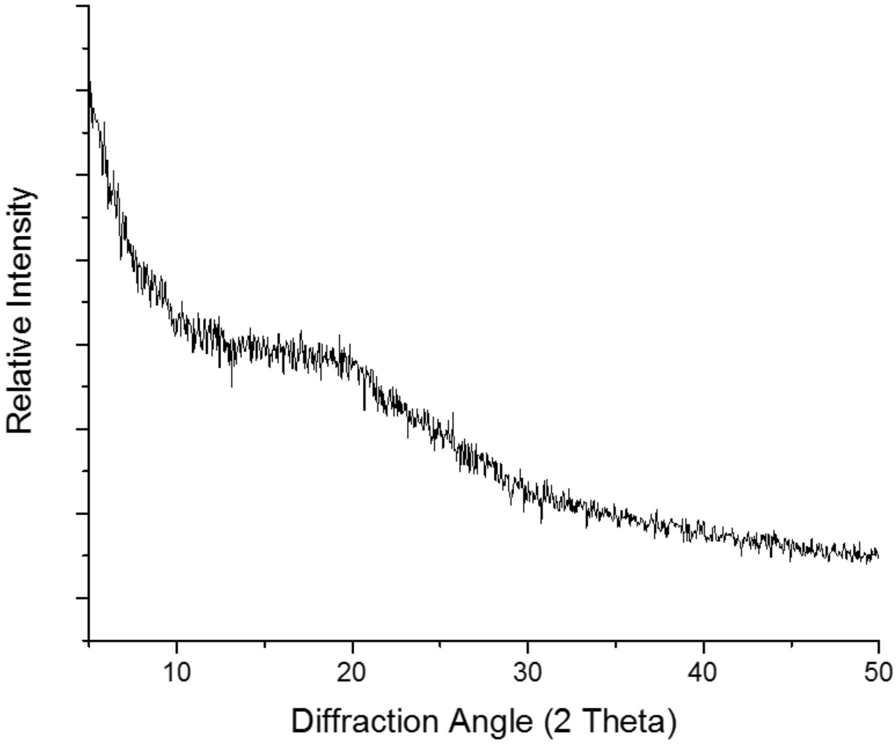


Figure S3. Powder X-ray diffraction (PXRD) pattern of **CalP**.

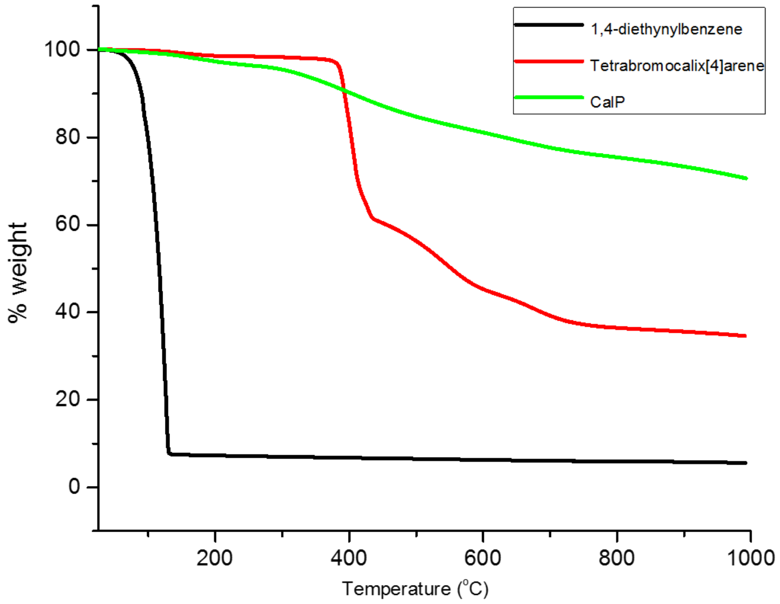


Figure S4. TGA plots for **CalP** (green) and monomers 1,4-diethynlebenzene (black) and tetrabromocalix[4]arene (red).

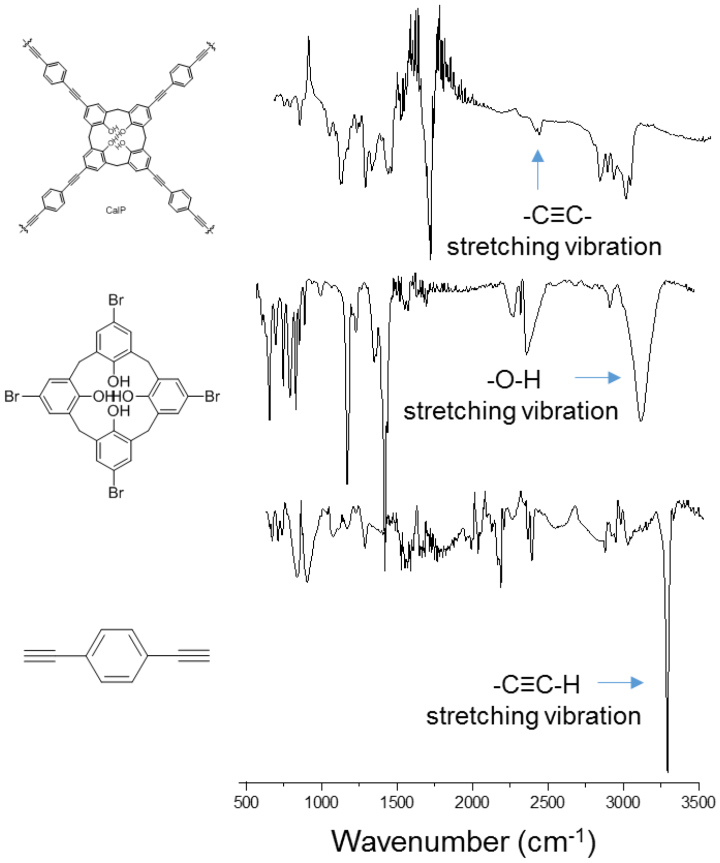


Figure S5. FTIR spectra of **CalP** and corresponding monomers.

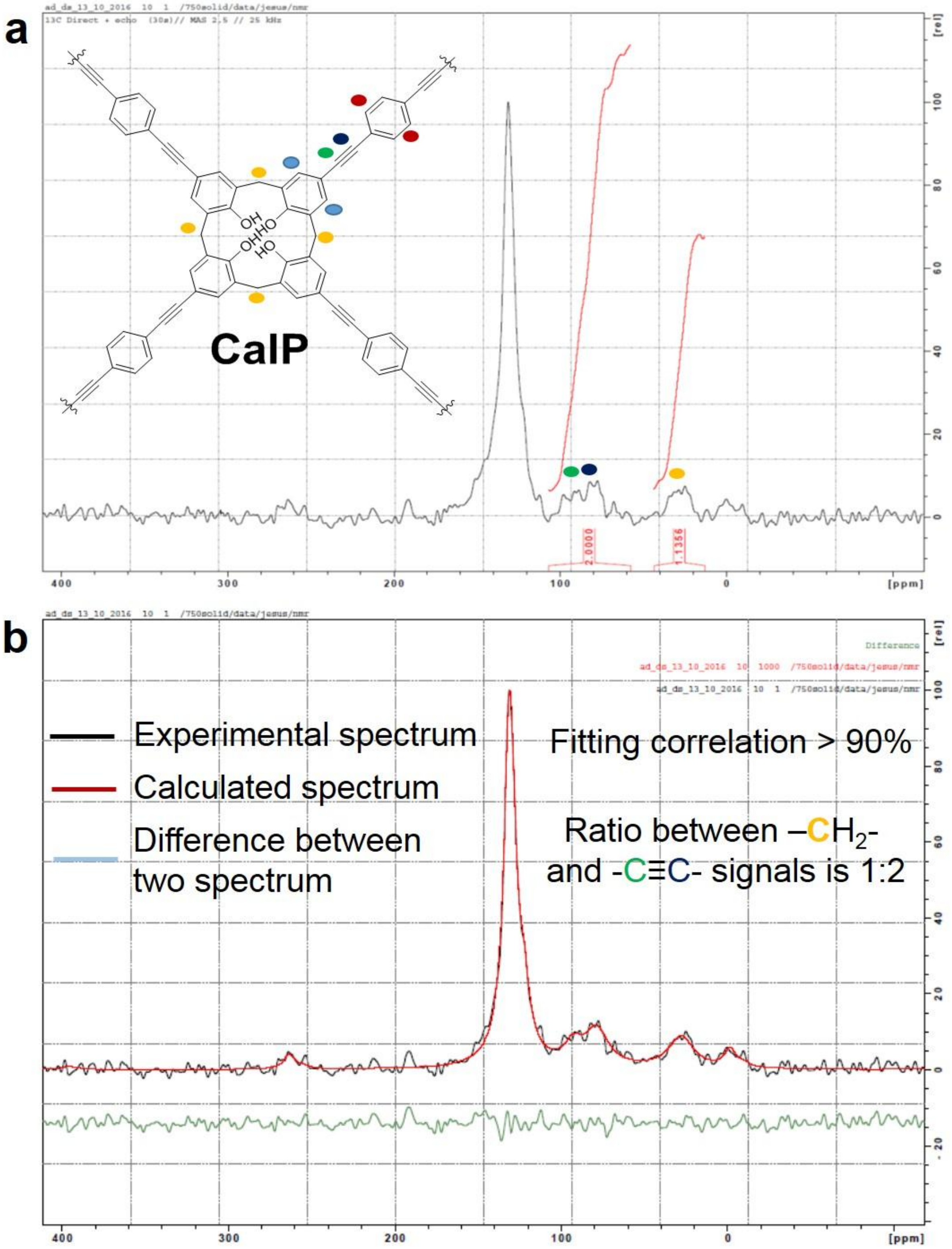


Figure S6. ^{13}C DP/MAS NMR spectrum of **CalP**. (a) Experimental spectrum with peak assignments indicated by color and with peaks of interest integrated. (b) Overlap of experimental and calculated spectra of **CalP** that have a fitting correlation of over 90%.

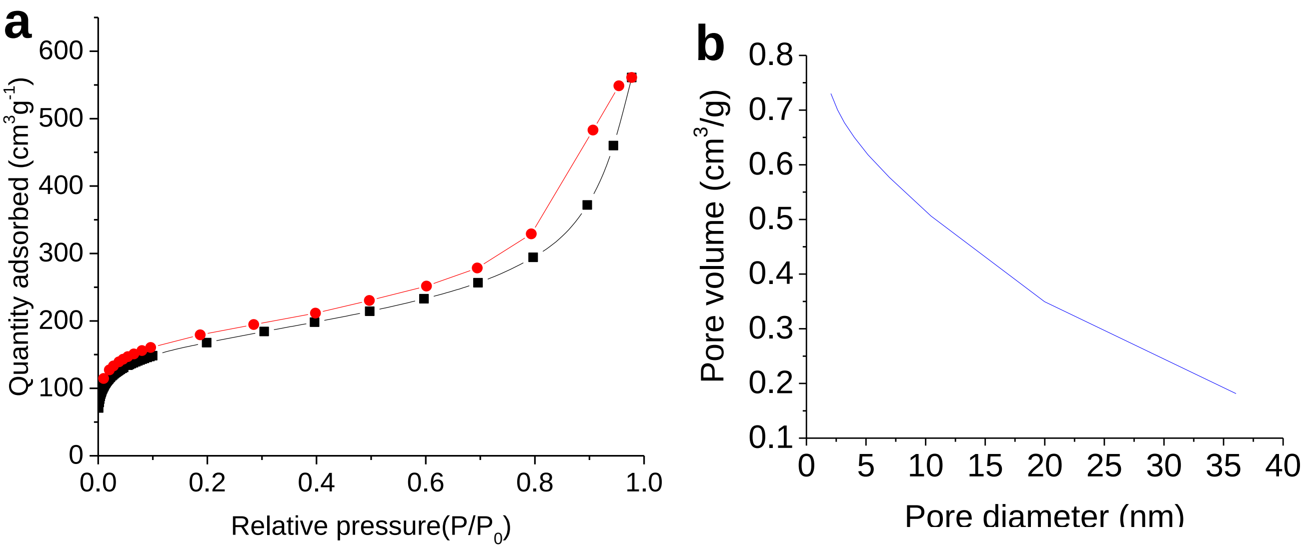


Figure S7. (a) N_2 uptake isotherms at 197 K (black squares and red circles represent adsorption and desorption values, respectively); calculated surface area = 596 m^2 g^{-1}. (b) BJH pore size distribution.

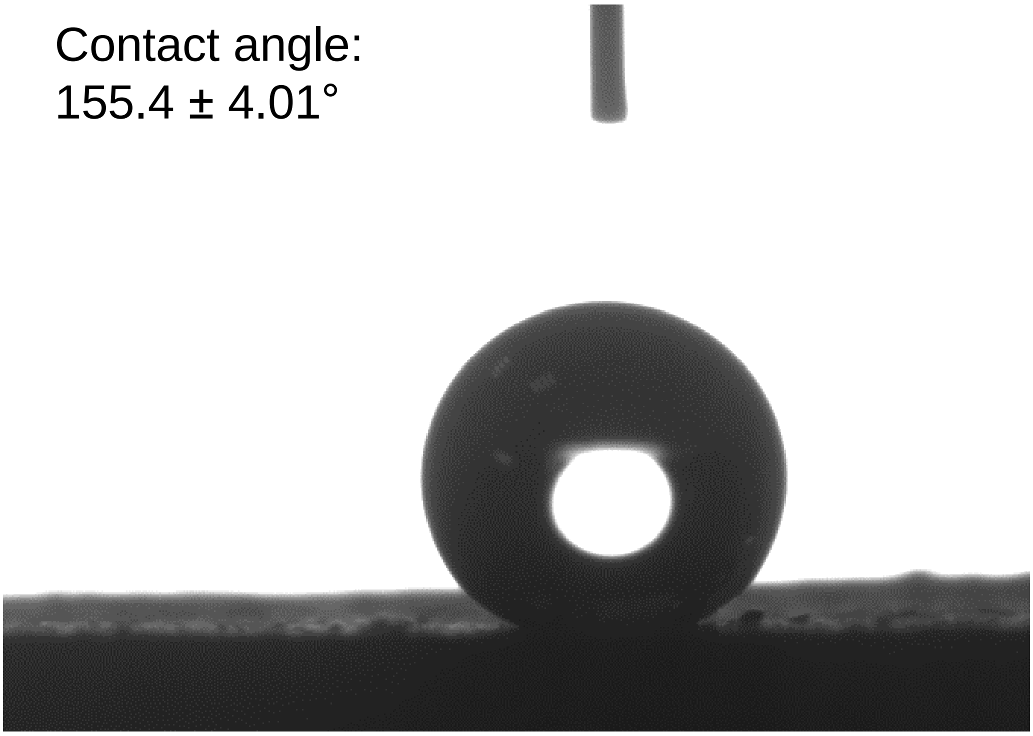


Figure S8. Superhydrophobic behavior of the **CalP**-coated surface. A sessile water droplet (7.0 µL) sitting on a **CalP** surface has a contact angle of 155.4 ± 4.01°.

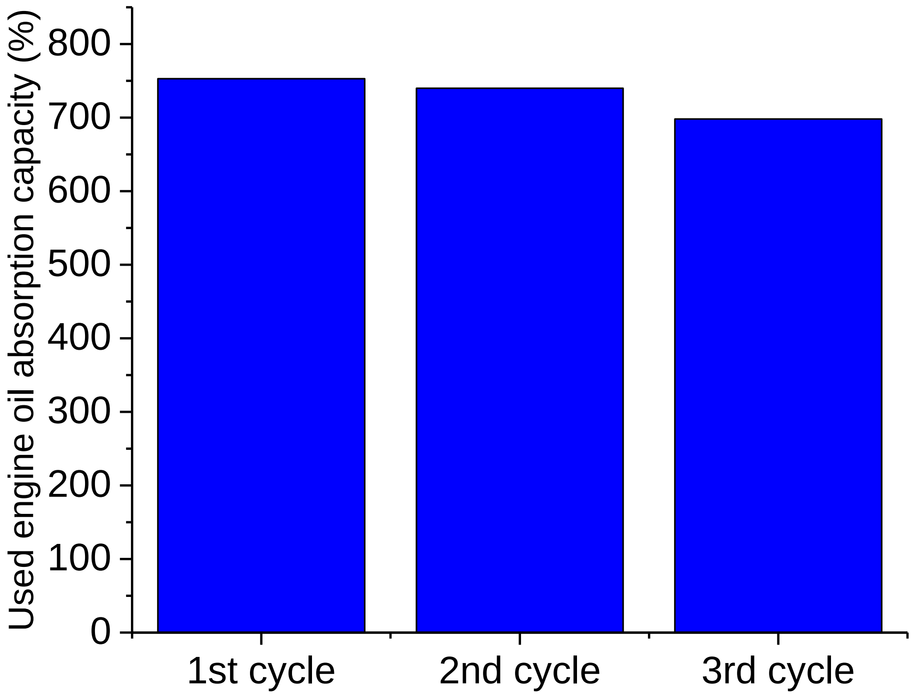


Figure S9. Variation of the absorption capacity for used engine oil; oil can be absorbed at least 3 times with only a slight decrease in uptake capacity.

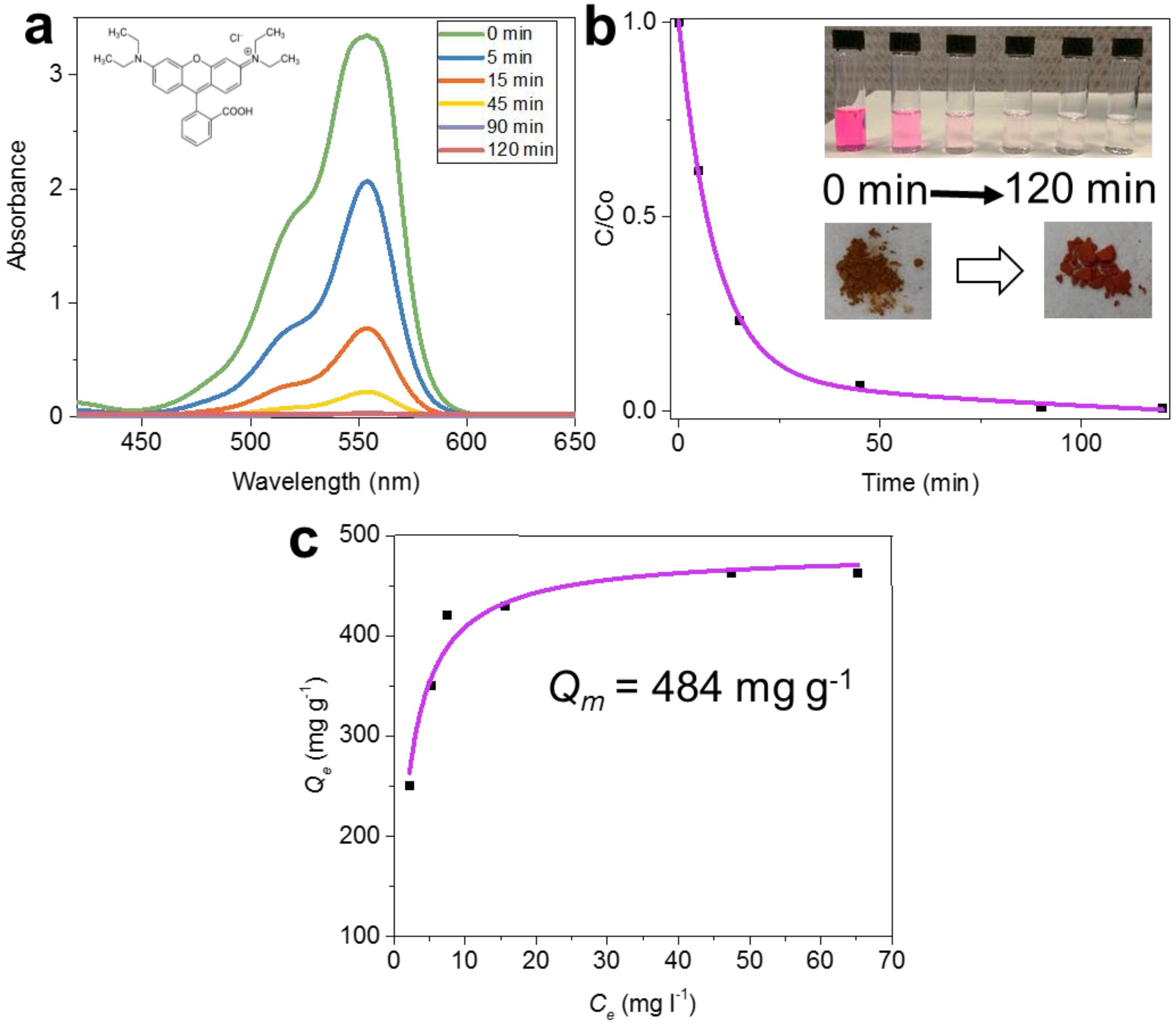


Figure S10. (a) UV–Vis absorption spectra of an aqueous solution of RhB (239 mg/L, 10 ml) in the presence of **CalP** over time. Inset (left) shows the molecular structure of the dye. Legend (right) correlates spectrum color with time. (b) Plot of the decrease in concentration of RhB due to the removal of the dye from solution by **CalP**. Inset (top) shows the fading color of the solution as the dye is absorbed. Inset (bottom) shows **CalP** before and after absorption of RhB. (c) Isotherm corresponding to the absorption of RhB on **CalP**. Q_e (mg g^{-1}) is the amount of dye absorbed at equilibrium, C_e (mg l^{-1}) is the equilibrium solute concentration.

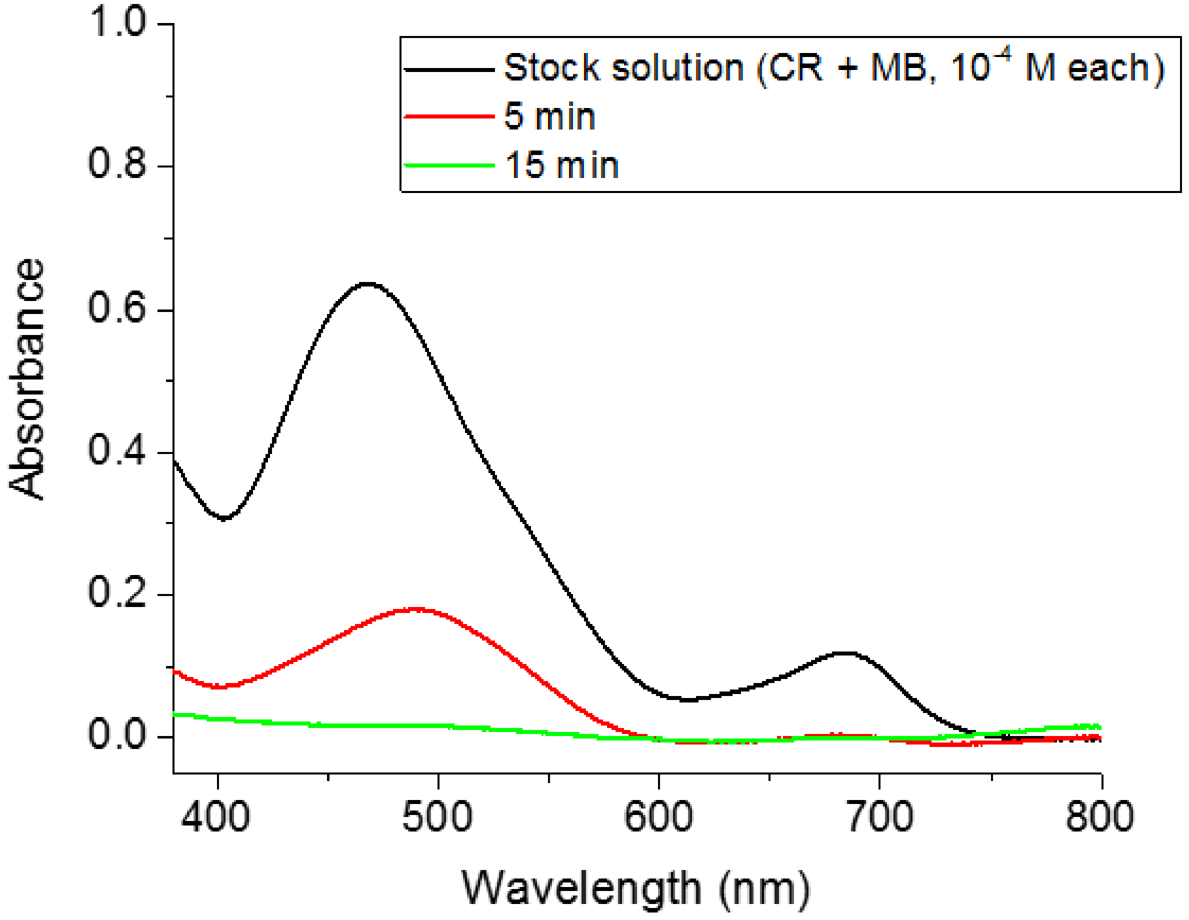


Figure S11. UV–Vis absorption spectra of a 1 N NaCl solution of MB and CR (0.25×10^{-4} M each, 10 ml) in the presence of **CalP** (5 mg) over time.

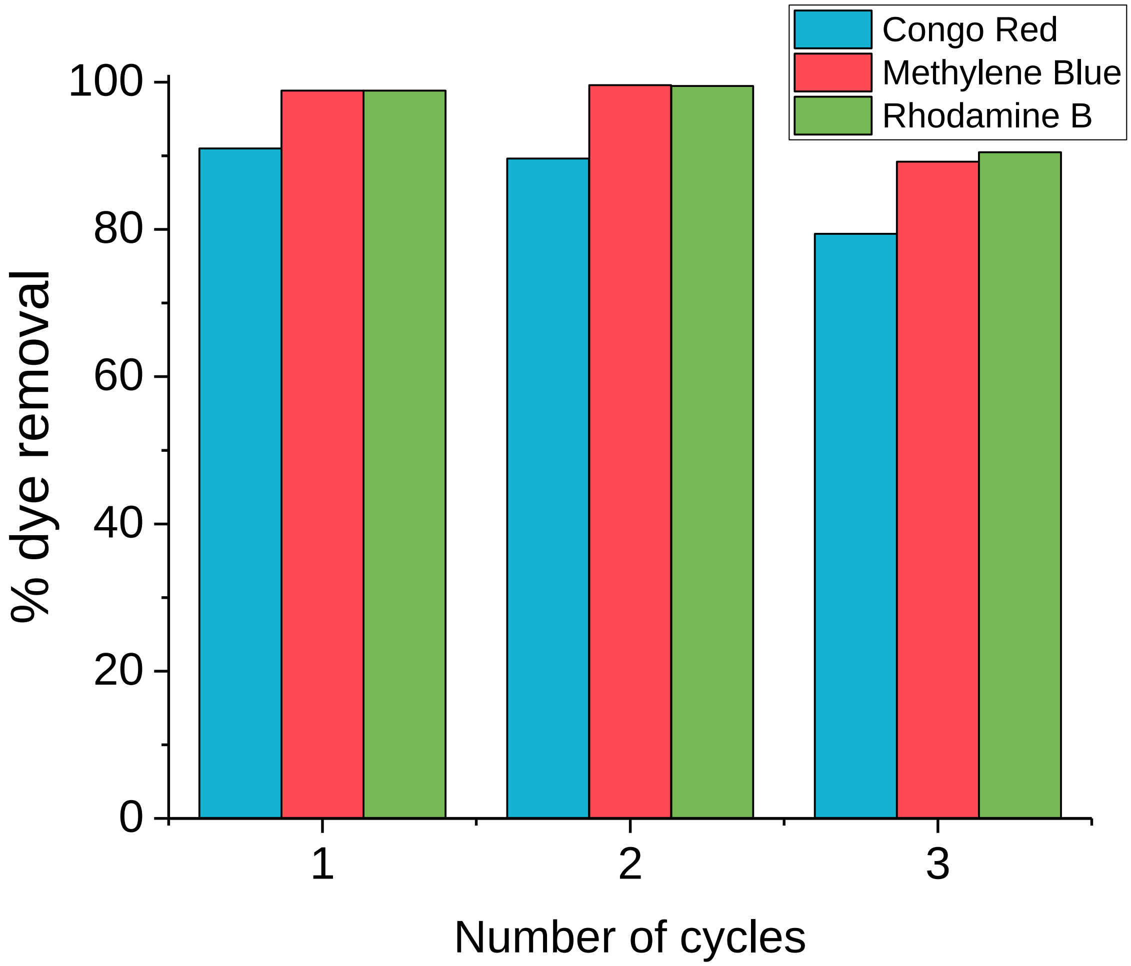


Figure S12. Recycling of **CalP** for toxic dye absorption; dyes (Congo red, methylene blue and rhodamine B) could be removed three times with only a slight decrease in absorption capacity.

References:

1. X. Wang, Y. Zhong, T. Zhai, Y. Guo, S. Chen, Y. Ma, J. Yao, Y. Bando and D. Golberg, *J. Mater. Chem.*, 2011, **21**, 17680-17687.