

Targeted Design of Dual-Functional Metal Organic Frameworks (DF MOFs) as a Highly Efficient Sorbent for Hg²⁺ Ions: Synthesis for Purpose

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Experimental Section

Materials and Physical Techniques

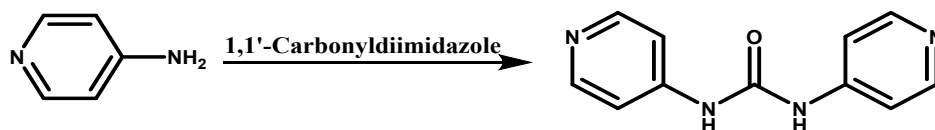
All starting materials, including Zinc(II) nitrate hexahydrate, 1,1'-Carbonyldiimidazole, 4-Aminobenzoic acid and 4-aminopyridine were purchased from Aldrich and Merck Company and used as received. Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were recorded using Thermo Nicolet IR 100 FT-IR. The thermal behavior was measured with a PL-STA 1500 apparatus with the rate of 10°C.min⁻¹ in a static atmosphere of argon. X-ray powder diffraction (XRD) measurements were performed using a Philips X'pert diffractometer with monochromated Cu-K α radiation. The ¹H-NMR spectrum was recorded on a Bruker AC-250 MHz spectrometer at ambient temperature in d₆-DMSO and D₂SO₄. The samples were also characterized by field emission scanning electron microscope (FE-SEM) SIGMA ZEISS and TESCAN MIRA with gold coating.

Synthesis

Synthesis of ligand L2

4-aminopyridine (0.941 g, 10 mmol) was dissolved in 25 mL of dry THF. To this solution, 1,1'-Carbonyldiimidazole (0.97 g, 6 mmol) was added. The mixture was refluxed under argon atmosphere overnight. The mixture was cooled to room temperature and the solvent was removed

in vacuo. The resulting residue was taken up in brine and washed several times with distilled water and dried in vacuo to give white precipitate.



Spectroscopic data:

FT-IR (KBr pellet, cm^{-1}): 3394-2938 (vs), 2490 (m), 2283 (w), 2221 (m), 1734 (s), 1591 (vs), 1505 (vs), 1420 (m), 1331 (m), 1283 (s), 1188 (vs), 1000 (m), 826(s), 732 (w), 524 (w). Anal. calcd for $\text{C}_{11}\text{H}_{10}\text{N}_4\text{O}$: C, 61.67; H, 4.71; N, 26.15, Found: C, 60.58; H, 4.64, N: 26.28. MS (m/z): 214.10 (M^+ , base peak). $^1\text{H-NMR}$ (d_6 -DMSO) 9.29 (2H, s), 8.37-8.38 (4H, d), 7.43-7.44 (4H, d).

Synthesis of the ligand N1, N3-di(pyridine-4-yl) malonamide (S)

The S spacer was synthesized by mixture of 0.07gr malonyl dichloride (0.5mmol) and 0.09gr of 4-amino pyridine (1mmol) in 40cc dry THF. After adding 8cc TEA (Triethylamine), put the mixture be refluxed in Ar condition for 24h. The resulting brown suspension was filtered, dried under ambient conditions, and poured into an aqueous saturated solution of Na_2CO_3 (50 ml). The resulting light brown solid was finally filtered and dried, obtaining the pure ligand S in ca. 73 % yield.

Synthesize of (TMU-32)

0.298 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol), 0.258 g of oba (1 mmol) and 0.214 g of L2 (1 mmol) were dissolved in 15 ml of *N,N'*-Dimethylformamide (DMF). The mixture was then placed in Teflon-lined stainless steel autoclaves and heated to 100 °C for 3 days. The mixture was then gradually cooled to room temperature over 48 hours. Colorless crystals were formed on the walls of the container with a 45% synthesis yield. FT-IR data (KBr pellet, cm^{-1}): selected bands: 3359 (w), 2929 (w), 1665 (vs), 1599 (s), 1518 (s), 1382 (m), 1303 (w), 1182 (m), 1022 (w), 841 (w), 783 (w), 535 (w). Anal. calcd for $\text{C}_{29}\text{H}_{27}\text{N}_7\text{O}_7\text{Zn}$: C, 53.51; H, 4.18; N: 15.06, found: C, 53.58; H, 4.32, N: 15.14.

Activation method

For activation purpose, synthesized crystals were soaked in a 15 mL of CH_3CN solvent for 4 days, with fresh CH_3CN added every 12 hours. After 4 days the CH_3CN solution was decanted, and vacuum-dried at 60°C for 4 h.

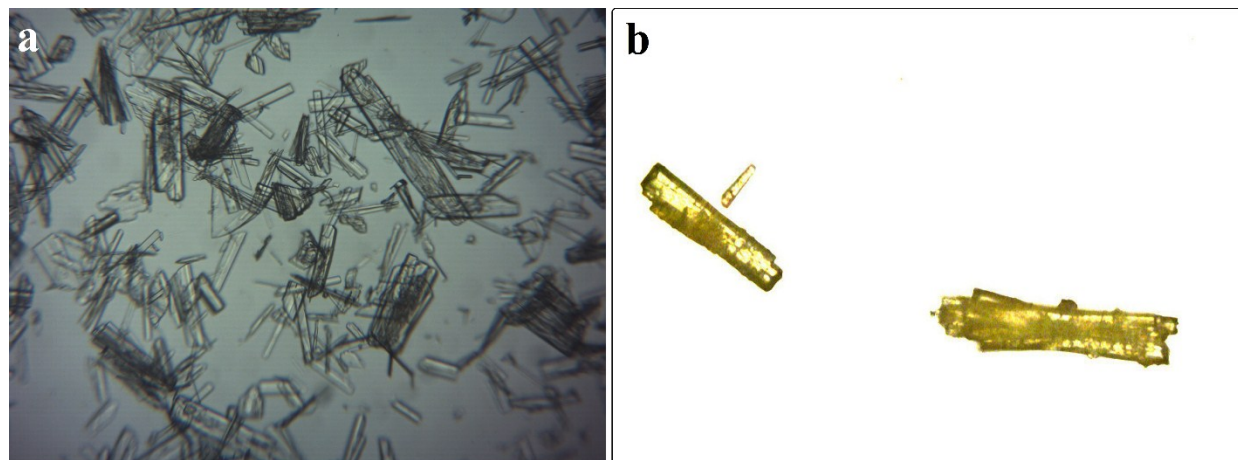
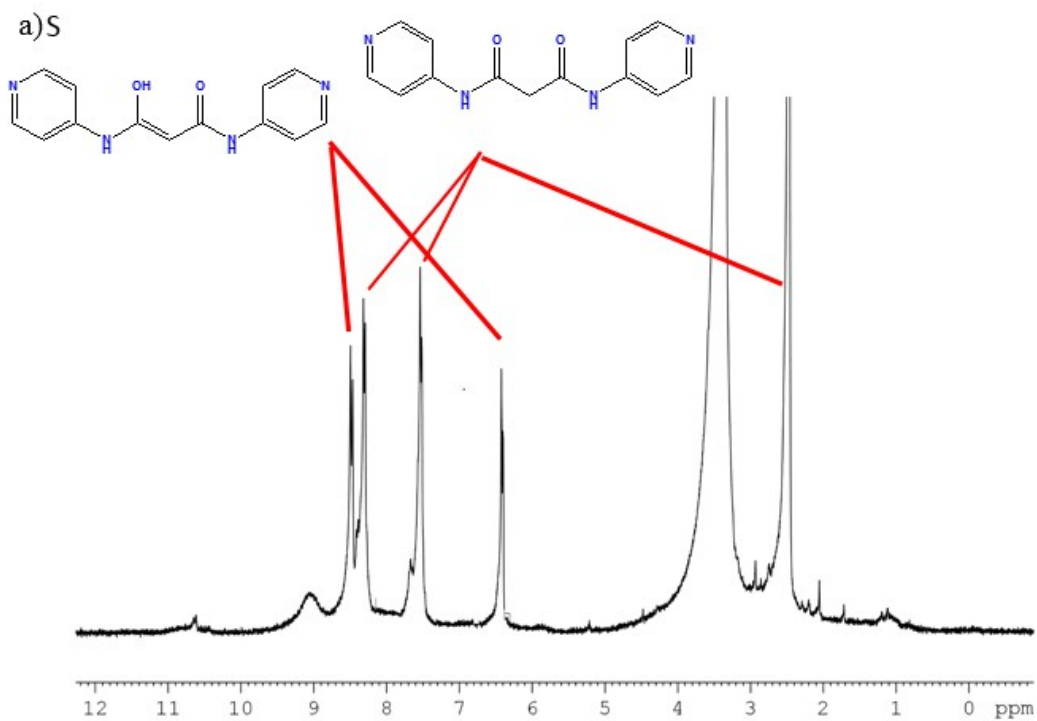


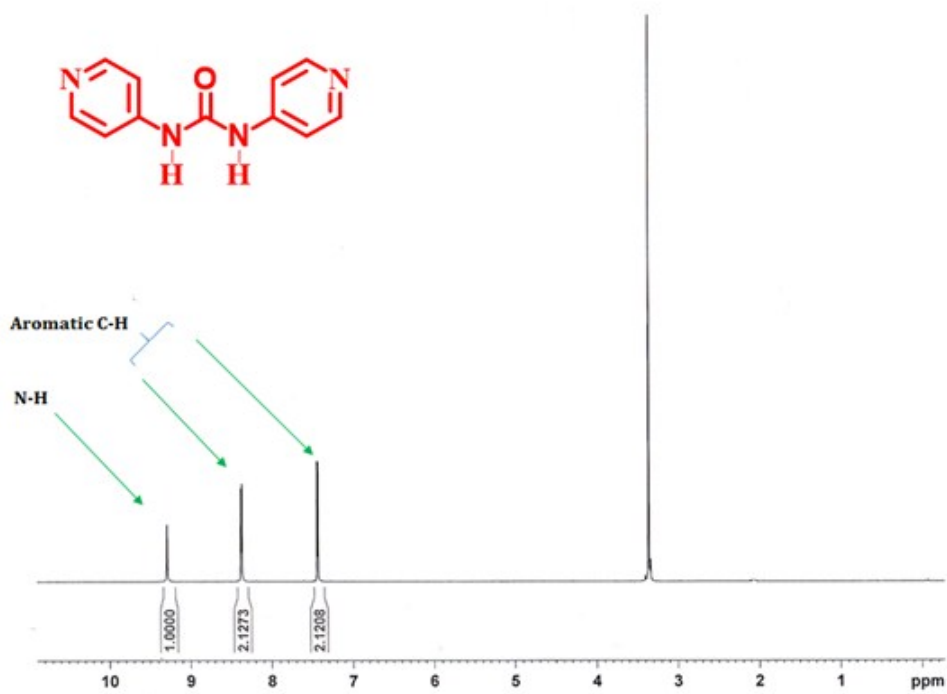
Fig.S1: From left to right: color of parent crystal TMU-32 changed from with into light brown in daughter samples TMU-32S *via* S.

NMR of parent MOFs and SALE samples

Approximately 5 mg of each MOF was placed in an NMR tube and dissolved in $100\ \mu\text{L}$ of D_2SO_4 and 0.6 mL of d_6DMSO by sonication. Once a homogeneous solution was obtained, the ^1H NMR spectra were obtained.



b)



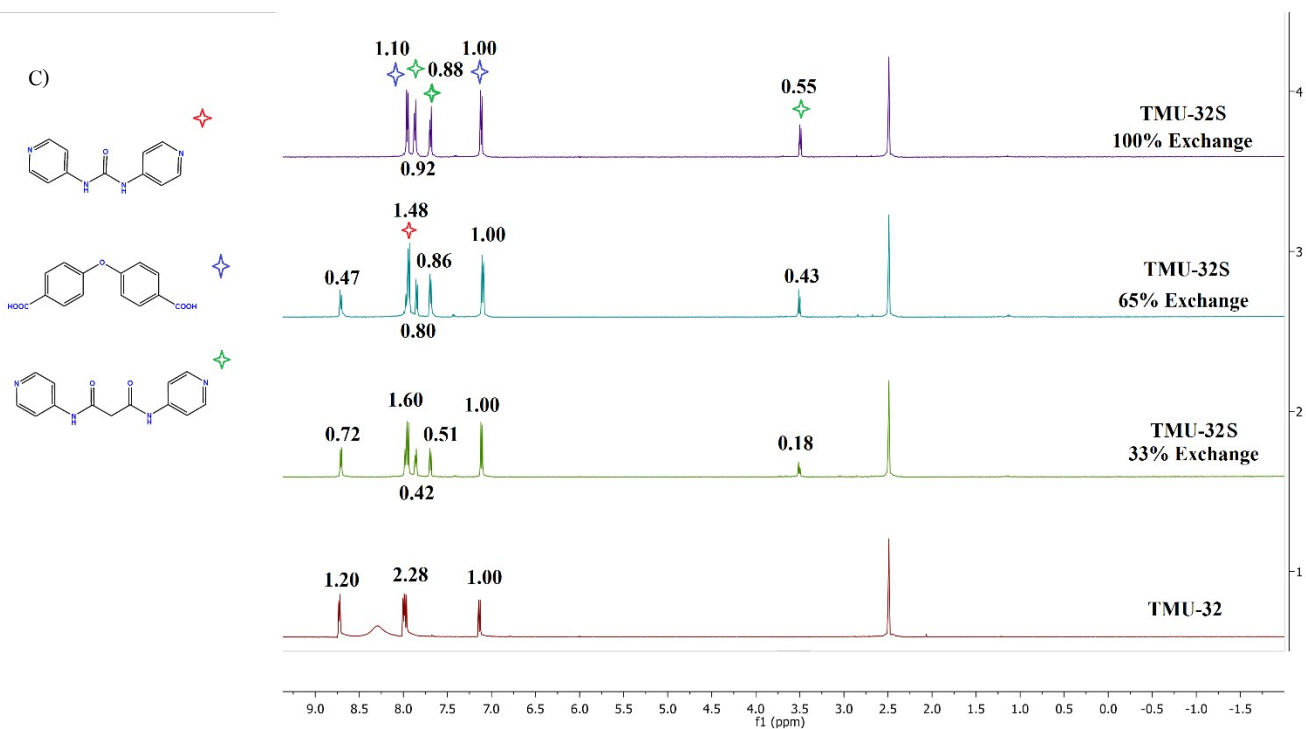


Fig.S2: NMR spectrum of a) S malonamide linker in DMSO b) urea linker in DMSO and c) compound TMU-32, 32S 33%, 32S 65% and 32S 100% decomposed by D_2SO_4

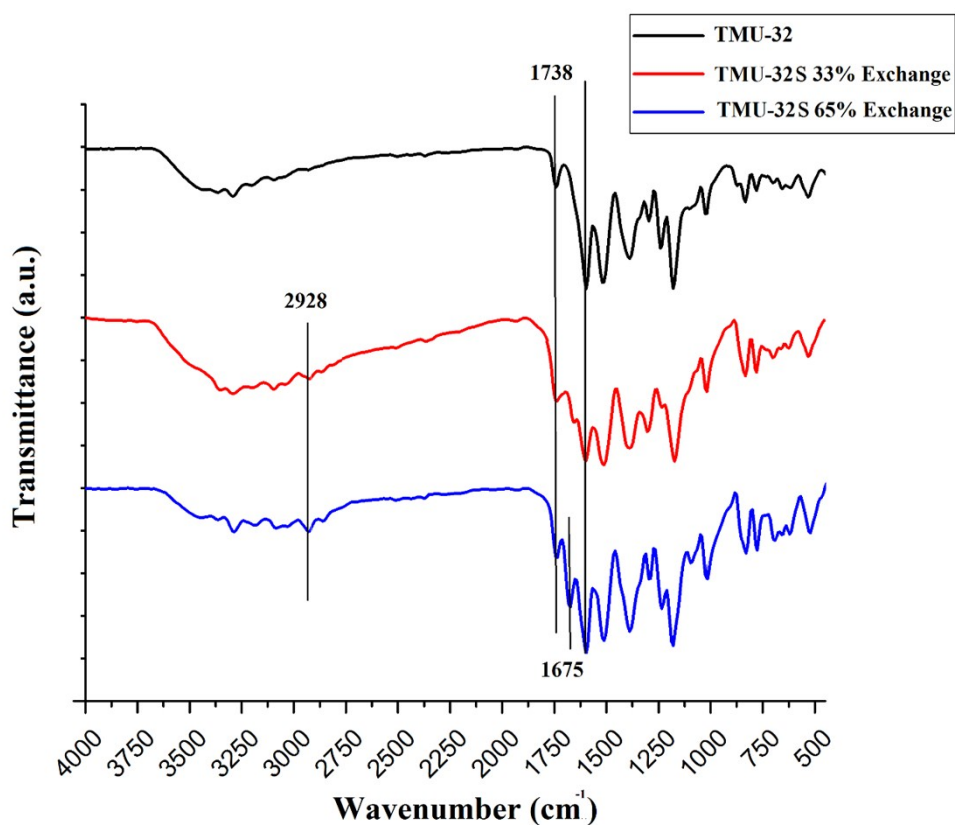


Fig. S3: IR spectroscopy of the TMU-32 (black), TMU-32S (35%) and TMU-32S (65%)

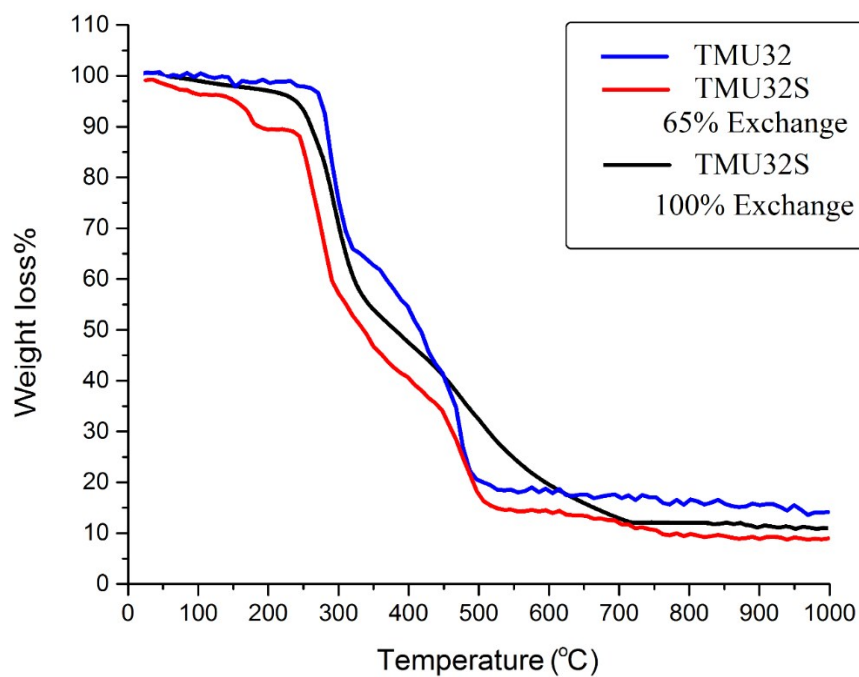


Fig. S4: Thermal gravimetric analysis of TMU-32, 32S 65% and 32S 100% after activation

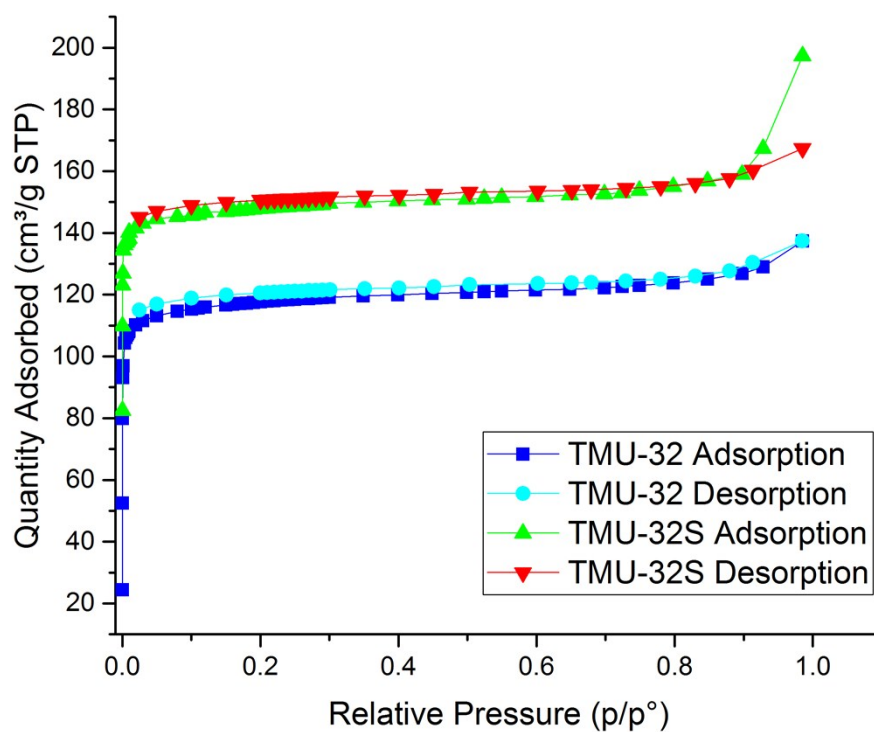


Fig. S5: Nitrogen adsorption-desorption isotherms at 77 K of TMU-32 and TMU-32S

Hydrophilicity of TMU-32:

The incorporation of hydrophilic urea functional groups into the TMU-32 backbone imparts a hydrophilic character to the framework structure which, therefore, makes it a suitable platform for applications in aqueous environments. An interesting contrast can be observed when comparing the miscibility of MOF in water phase with its behavior in organic (toluene and dichloromethane) phase. Due to the hydrophilicity, TMU-32 prefers the aqueous phase rather than the organic one.

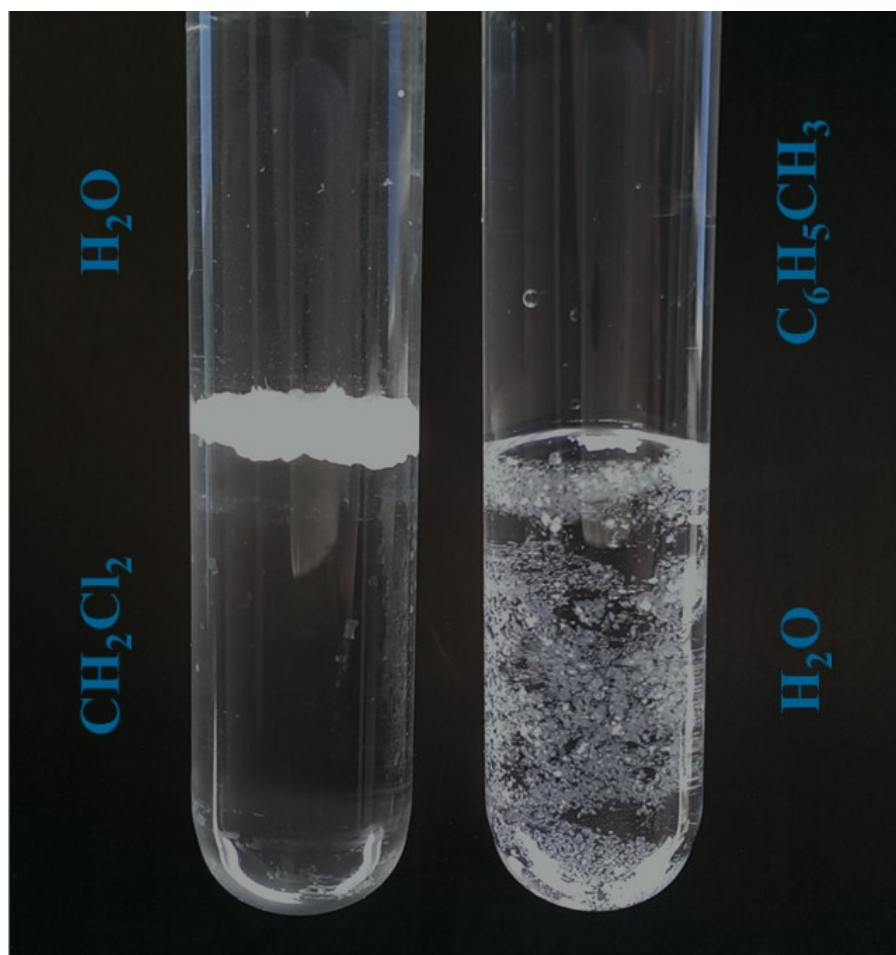


Fig.S6: Hydrophilicity of TMU-32 in two solvents



Fig.S7: Contact angle measurement on **TMU-32**

Adsorption isotherm study

To study the adsorption isotherm, 7 mg of activated sorbent was added to 100 ml of Hg(II) solution with different initial concentrations varying from 50 to 300 ppm and stirred for 20 min at room temperature. Then, the mixture was centrifuged at 14000 rpm for 5 min, and the remaining concentration of Hg(II) was determined via ICP. The total amounts of Hg(II) on the TMU-32, 32S and the removal efficiency were calculated from equations 1 and 2, respectively:

$$Q_t = \frac{(C_0 - C_t)V}{m} \quad (S1)$$

$$\%R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (S2)$$

In these equations, C_0 and C_e point to the initial and equilibrium concentrations of Hg(II) ions (mg.L^{-1}), respectively, V referred to the volume (L) of samples and m considered as the adsorbent mass (g).

A monolayer adsorption is defined with linear (S3) and nonlinear Langmuir (S4) model upon the homogeneous surface of the adsorbent and represented as:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \quad (\text{S3})$$

$$q_t = \frac{kq_m C_e}{1 + kC_e} \quad (\text{S4})$$

Where C_e (mg.L^{-1}) is the ion concentration at equilibrium, q_m (mg.g^{-1}) points to the maximum sorption capacity obtained for monolayer sorption, b (L.mg^{-1}) is devoted to the energy of sorption process.

Adsorption kinetics study

7 mg of TMU-32 and 32S was added into a glass beaker containing 100 ml of 100 ppm Hg^{2+} solution. At different times (1 to 120 min), the adsorption process was stopped and sampling was done. Then, the mixture was filtered through a $0.22 \mu\text{m}$ membrane filter and the filtrate was applied for determining the residual concentration of Hg^{2+} ions by ICP-OES spectrometer.

Linear (S5) and nonlinear (S6) Kinetic model equations used to investigate Hg (II) removal:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t \quad (\text{S5})$$

$$q_t = \frac{kq_e^2 t}{1 + kq_e t} \quad (\text{S6})$$

Where Q_t (mg.g^{-1}) is the total amount of Hg^{2+} ions adsorbed at time t (min), C_0 and C_t are the initial and equilibrium Hg^{2+} concentrations (mg.L^{-1}) at time t (min), respectively. V (L) is the volume of solution and m (g) is the adsorbent mass.

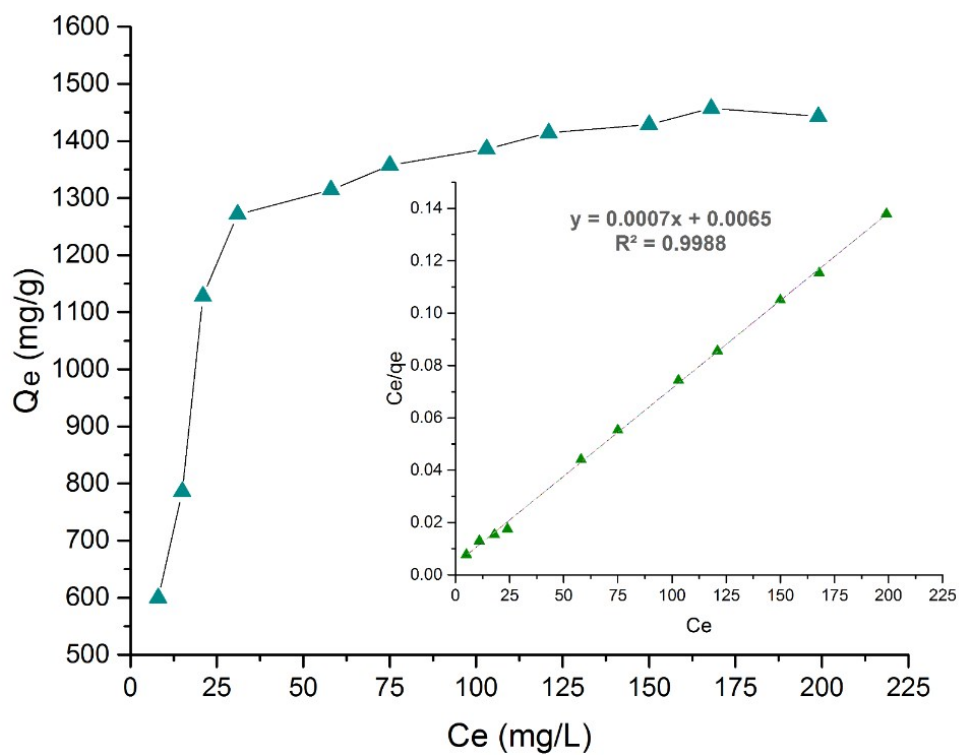


Fig. S8. Linear curves fitting with Langmuir and Hg^{2+} ion.

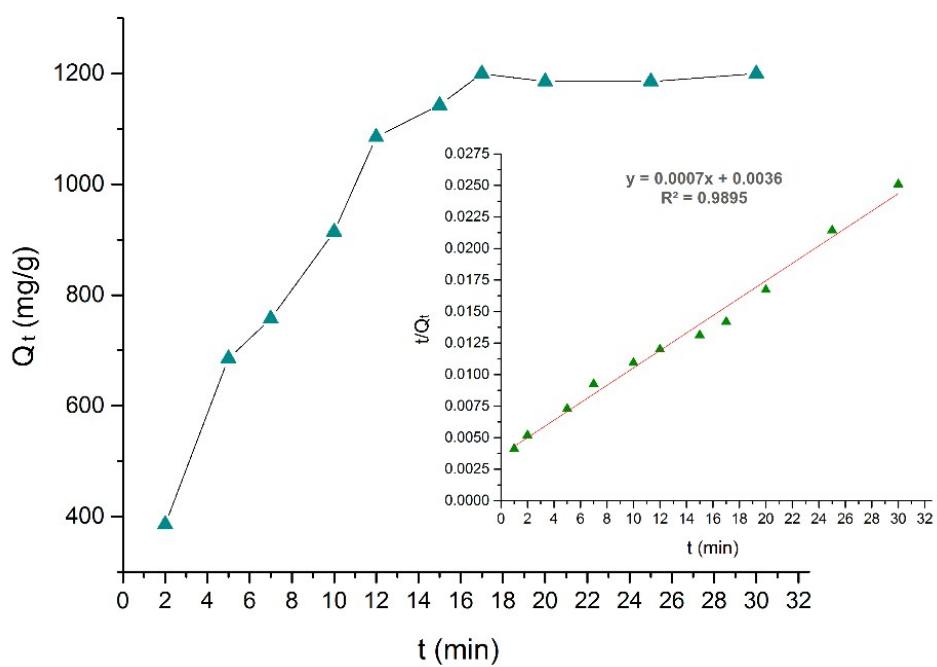


Fig.S9: Linear pseudo-second-order kinetics model of $\text{Hg}(\text{II})$ adsorption on TMU-32S 65%.

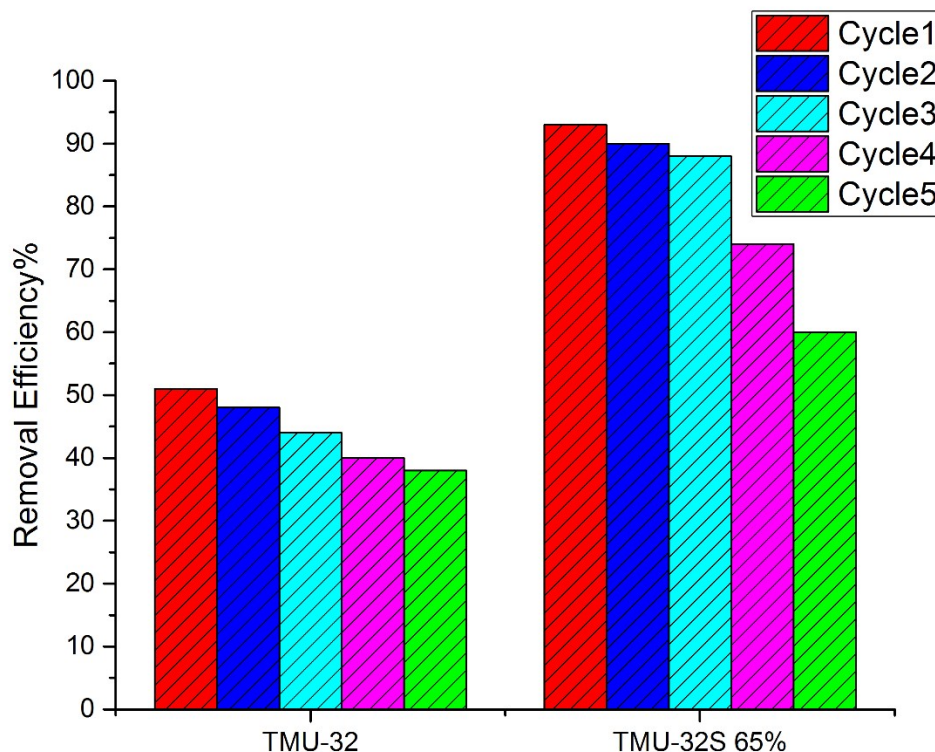


Fig.S10: Adsorption-desorption cycles of TMU-32 and TMU-32S 65%.

The removal efficiency for regeneration test was calculated from equation:

$$\%R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (S2)$$

Where C_o (mg/L) is the initial metal concentration, C_e (mg/L) is the concentration of metal remaining in the stock solution after the adsorption process.

Number of cycles	TMU-32		TMU-32S 65%	
	C_e	$\%R$	C_e	$\%R$
Cycle1	49	51	7	93
Cycle2	52	48	10	90
Cycle3	55	45	12	88
Cycle4	60	40	25	75
Cycle5	61	39	41	59

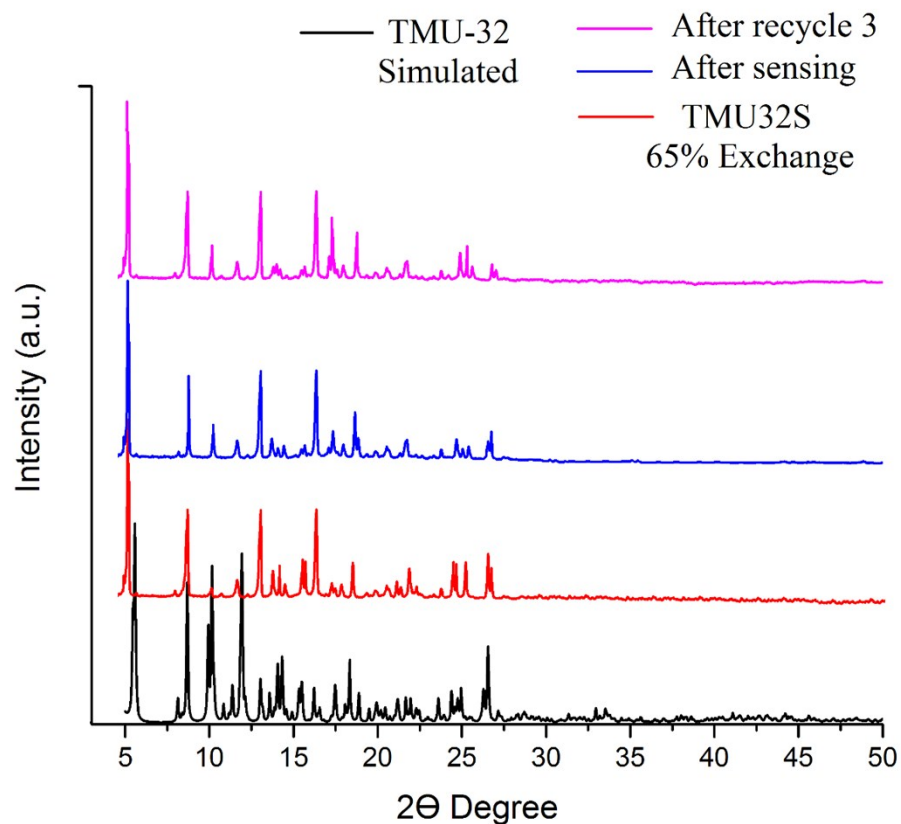


Fig.S11: PXRD patterns of simulated TMU-32, as-synthesized, after sensing and after recycle of TMU-32S

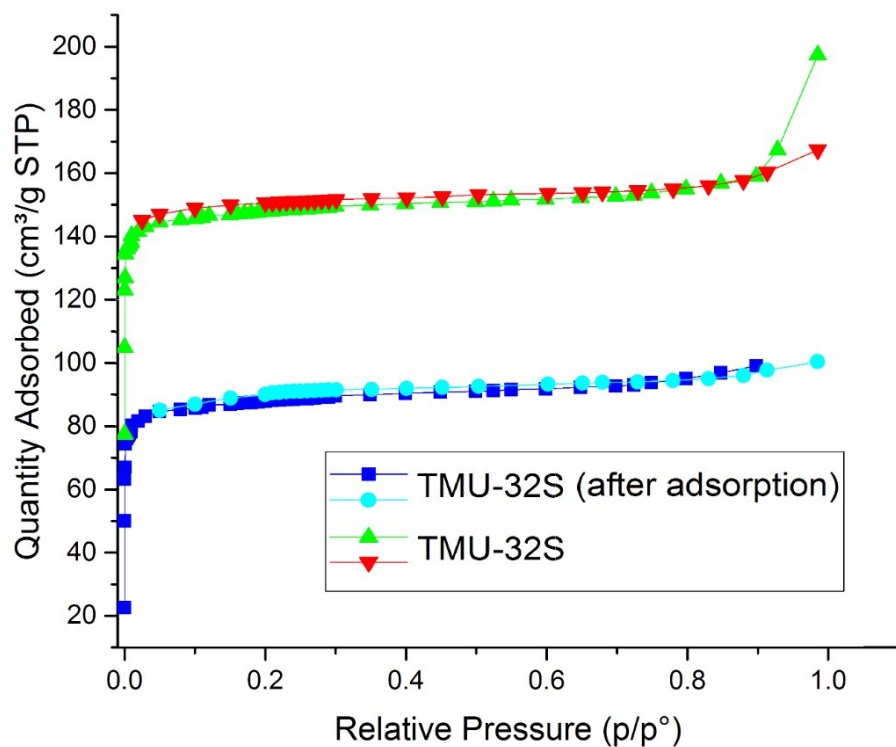


Fig.S12: Nitrogen adsorption-desorption isotherms at 77 K for TMU-32S after Hg²⁺ adsorption

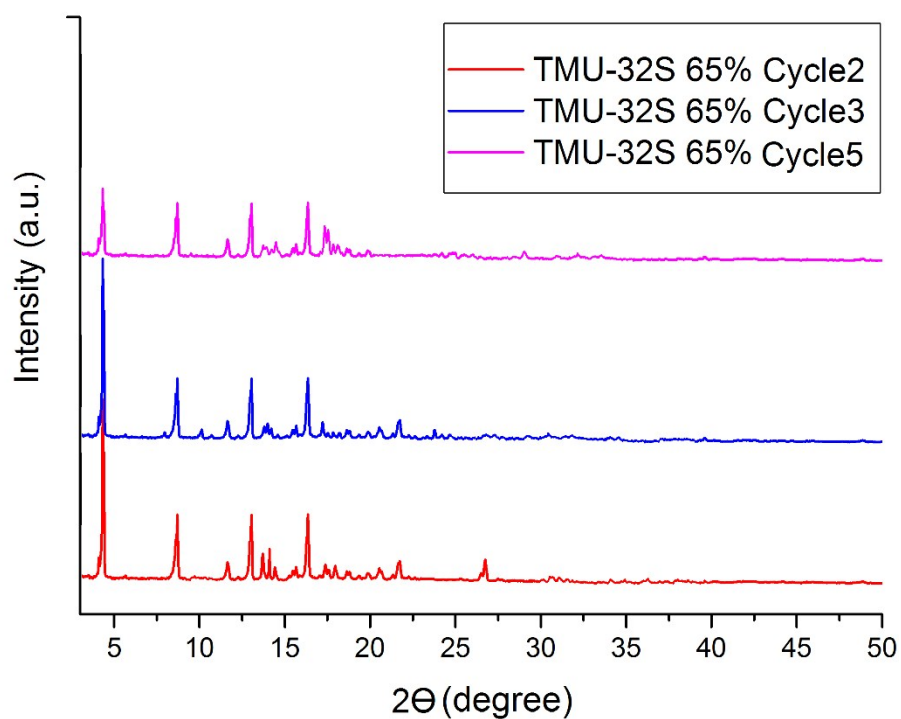


Fig.S13: PXRD patterns of TMU-32S after each recycle

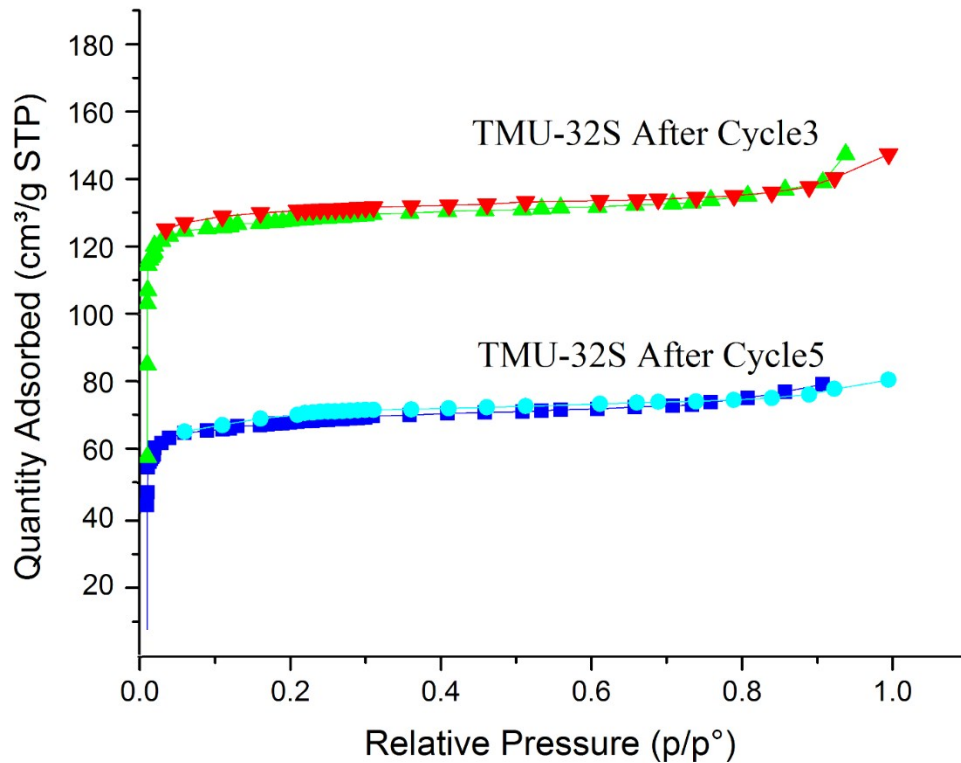


Fig.S14: Nitrogen adsorption-desorption isotherms at 77 K for TMU-32S after recycle3 and Recycle5.