Support Information

Tailored Adsorption Properties of Imidazole-Based Halogen Bonded Organic Frameworks for Anionic Dye Removal

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Table of Contents

1. Materials and Methods

All starting materials and solvents were obtained from commercial suppliers and used without further purification. Analytical thin-layer chromatography (TLC) was performed on silica-gel plate w/UV254 (200 μm). The ^{1}H NMR spectra were recorded on 600 MHz spectrometer (Bruker AVANCE NEO 600 spectrometer) in the indicated solvents. Chemical shifts are expressed in parts

per million (δ) using residual solvent protons as internal standard. The couple constants values (J) are in Hertz (Hz). The following abbreviations were used for signal multiplicities: s, singlet; d, doublet. Solid-state diffuse reflectance UV-vis spectra characterized by Lambda 750S. Powder XRD patterns were recorded on Rigaku SmartLab SE diffractometer (CuKα, λ = 1.5405 Å, 45 kV, 200 mA). Scanning electron microscopy (SEM) images were recorded on field emission scanning electron microscope (Tescan CLARA). X-ray photoelectron spectroscopy (XPS) was performed in ESCALAB 250Xi (The adventitious carbon located at 284.8 eV was used to calibrate samples without the carbon themselves). The morphologies of materials were characterized using field emission transmission electron microscopy (FE-TEM, F200).

2. Synthesis
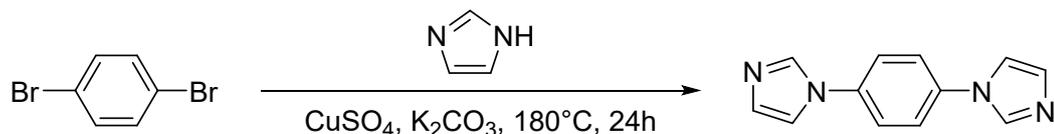
Scheme S1.Synthesis of **DIB**

Synthesis of 1,4-di(1H-imidazol-1-yl)benzene (DIB):

1,4-Dibromobenzene (2.0 g, 8.5 mmol), imidazole (2.4 g, 35.6 mmol), K_2CO_3 (3.75 g, 27.2 mmol), and $CuSO_4$ (0.027 g, 0.17 mmol) were combined in a Schlenk tube and purged with nitrogen. The reaction mixture was heated and stirred at 180°C for 24 hours. After cooling to room temperature, the reaction mixture was thoroughly washed with water. The crude product was dissolved in ethanol (90 mL) and the organic layer was separated. The organic layer was evaporated to dryness, yielding the crude product. The residue was recrystallized from a mixture of water and methanol to afford a white solid, which was dried under vacuum. Yield: 1.43 g (82%). ^1H NMR (DMSO-d_6, 600 MHz). δ (ppm): 8.34 (s, 2H), 7.82 (s, 4H), 7.82 (s, 2H), 7.13 (s, 2H).
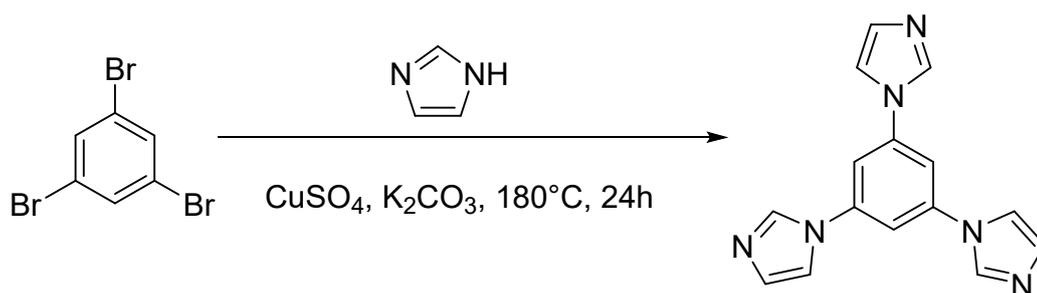
Scheme S2.Synthesis of **TIB**

Synthesis of 1,3,5-tri(1H-imidazol-1-yl)benzene (TIB):

Imidazole (2.72 g, 34.0 mmol), 1,3,5-tribromobenzene (1.26 g, 4.00 mmol), K_2CO_3 (2.21 g, 15.99 mmol), and $CuSO_4$ (0.025 g, 0.16 mmol) were combined in a Schlenk tube and purged with nitrogen. The reaction mixture was heated

at 180°C for 24 hours. After cooling the flask to room temperature, the reaction mixture was thoroughly washed with water. The resulting solid was added to methanol (100 mL) and the solution was filtered to remove the dark brown residue. The white product precipitated from methanol upon the addition of water, and the solid was filtered and dried under vacuum. Yield: 0.76 g (69%). ^{1}H NMR (DMSO-d_6, 600 MHz). δ (ppm): 8.55 (s, 2H), 8.04 (s, 4H), 7.97 (s, 2H), 7.18 (s, 2H).

Preparation of 1-MMZ-Ag$^+$ and 1-MMZ-I$^+$
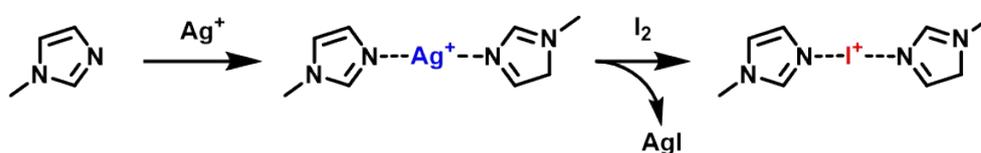
1-MMZ-Ag$^+$:

1-Methylimidazole (0.315 mL, 4 mmol) was dissolved in 3 mL of methanol. To this solution, AgBF4 (390 mg, 2 mmol) dissolved in 7 mL of methanol was added dropwise. The mixture was stirred at room temperature for 1 hour. The solvent was then removed under reduced pressure without heating, yielding a yellow solid, which was dried under vacuum.

1-MMZ-I$^+$:

1-Methylimidazole (0.315 mL, 4 mmol) was dissolved in 3 mL of methanol. To this solution, AgBF$_4$ (390 mg, 2 mmol) dissolved in 7 mL of methanol was added dropwise. The mixture was stirred at room temperature for 1 hour. Iodine (502 mg, 2 mmol) dissolved in 5 mL of methanol was then added to the reaction mixture, and the stirring was continued at room temperature in the dark for 1 hour. The silver iodide precipitate was filtered out to give the solution phase. The solvent was then removed under reduced pressure without heating until a small amount of solvent remained in the flask. An excess of diethyl ether was added to the flask until a solid precipitated. The flask was then refrigerated at

0°C for 2 hours. The resulting yellow solid was collected by filtration and dried under vacuum.

Preparation of MOP-DIB and XOP-DIB
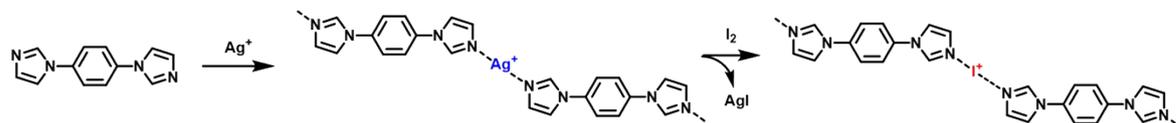
MOP-DIB:

DIB (21 mg, 0.1 mmol) was dissolved in 2 mL of methanol. To this solution, AgBF4 (20 mg, 0.1 mmol) dissolved in 1 mL of methanol was added dropwise. The mixture was stirred at room temperature for 1 hour. The solvent was then removed by filtration under reduced pressure, yielding a white solid, which was dried under vacuum overnight.

XOP-DIB:

DIB (21 mg, 0.1 mmol) was dissolved in 2 mL of methanol. To this solution, AgBF4 (20 mg, 0.1 mmol) dissolved in 1 mL of methanol was added dropwise. The mixture was stirred at room temperature for 1 hour. Iodine (26 mg, 0.1 mmol) dissolved in 1 mL of methanol was then added to the reaction mixture, and the stirring was continued at room temperature in the dark for 1 hour. The resulting mixture was filtered, and the solid was washed with petroleum ether to obtain a pale yellow solid, which was dried under vacuum overnight.

Preparation of MOF-TIB and XOF-TIB

MOF-TIB:

TIB (55.2 mg, 0.2 mmol) was dissolved in 2 mL of methanol. To this solution, AgBF4 (58.4 mg, 0.3 mmol) dissolved in 1 mL of methanol was added dropwise. The mixture was stirred at room temperature for 1 hour. The solvent was then

removed by filtration under reduced pressure, yielding a white solid, which was dried under vacuum overnight.

XOF-TIB:

TIB (55.2 mg, 0.2 mmol) was dissolved in 2 mL of methanol. To this solution, AgBF4 (58.4 mg, 0.3 mmol) dissolved in 1 mL of methanol was added dropwise. The mixture was stirred at room temperature for 1 hour. The solvent was then removed by filtration under reduced pressure. Iodine (76.1 mg, 0.3 mmol) dissolved in 2 mL of methanol was then added to the reaction mixture, and the stirring was continued at room temperature in the dark for an additional hour. The mixture was then sealed in a tube and heated at 150°C for 3 hours. The resulting brownish-yellow solid was collected by filtration, washed with petroleum ether, and dried under vacuum overnight.

3. Adsorption experiment

Adsorption experiment of dyes by XOF-TIB

10 mg of **XOF-TIB** was added to a UV cuvette containing 3 mL of a $4×10^{-5}$ M **MO/EBS/MB/NR** aqueous solution. The mixture was kept in the dark at room temperature for 24 hours. UV/Vis spectra were utilized to assess the adsorption capacity of **XOF-TIB** at specific time intervals.

10 mg of **XOF-TIB** was added to a UV cuvette containing 3 mL of a $4×10^{-4}$ M **CR** aqueous solution. The mixture was kept in the dark at room temperature for 24 hours. UV/Vis spectra were utilized to assess the adsorption capacity of **XOF-TIB** at specific time intervals.

Selective adsorption of dyes by XOF-TIB

10 mg of **XOF-TIB** was added to a UV cuvette containing 3 mL of a $4×10^{-5}$ **M**

MO and 4×10^{-5} M **MB** aqueous solution. The mixture was kept in the dark at room temperature for 24 hours. UV/Vis spectra were utilized to assess the adsorption capacity of **XOF-TIB** at specific time intervals.

10 mg of **XOF-TIB** was added to a UV cuvette containing 3 mL of a 4×10^{-4} **M CR** and 4×10^{-5} M **MB** aqueous solution. The mixture was kept in the dark at room temperature for 24 hours. UV/Vis spectra were utilized to assess the adsorption capacity of **XOF-TIB** at specific time intervals.

Dye release experiment after loading dye with XOF-TIB

10 mg of **XOF-TIB** loaded with **MO** were transferred to pure ethanol and Ethanol containing 1 mg NaCl, respectively. UV/Vis spectra were employed to measure release process of **MO** after certain time intervals.

Methods for Fitting and Calculating Parameters of Adsorption Kinetics and Isotherms

Adsorption Kinetics:

The pseudo-first-order model, where the adsorption rate is proportional to the number of unoccupied sites, is represented by the following equation:

$$\ln\left(q_e - q_t\right) = lnq_e - k_1 t \tag{1}$$

The pseudo-second-order model, where the adsorption rate is governed by chemical binding to active sites on the adsorbent surface, is epresented by the following equation:

$$\frac{1}{q_t} - \frac{1}{q_e} = \frac{1}{k_2 q_e^{\,2} t} \tag{2}$$

where q_t (mg g^{-1}) is the adsorption capacity of dye at time t (min), q_e is the adsorption capacity of dye at equilibrium, k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are

the adsorption rate constants of the two model, respectively.

Adsorption isotherms:

The Langmuir isotherm equation is expressed as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

The Freundlich isotherm equation is expressed as follows:

$$q_e = K_F C_e^{1/n} \tag{4}$$

where q_e (mg g^{-1}) is the adsorption capacity of dye at equilibrium, C_e (mg L^{-1}) is the concentration of dye in solution at equilibrium, q_m (mg g^{-1}) is the Langmuir maximum adsorption capacity, K_L (dm^3 mg^{-1}) is the Langmuir constant, K_F ((mg g^{-1}) (L mg^{-1})$^{1/n}$) is the Freundlich constant, and n indicates the Freundlich exponent.

Determination of the maximum adsorption capacity of XOF-TIB for anionic dyes

10 mg of **XOF-TIB** was added to 50 mL of 8×10^{-5} mol/L **MO** solution, and the mixture was continuously monitored using UV-Vis spectroscopy over time until no further changes were observed in the UV-Vis spectra, indicating the maximum adsorption capacity had been reached.

10 mg of **XOF-TIB** was added to 500 mL of 8×10^{-5} mol/L **EBS** solution, and the mixture was continuously monitored using UV-Vis spectroscopy over time until no further changes were observed in the UV-Vis spectra, indicating the maximum adsorption capacity had been reached.

10 mg of **XOF-TIB** was added to 500 mL of 4×10^{-4} mol/L **CR** solution, and the mixture was continuously monitored using UV-Vis spectroscopy over time until

no further changes were observed in the UV-Vis spectra, indicating the maximum adsorption capacity had been reached.

Reusability of XOF-TIB toward the adsorption of aqueous MO, EBS, and CR solutions.

After **XOF-TIB** reaches adsorption saturation for **MO/EBS/CR**, the solid is rinsed with ethanol until the eluent is clear. The resulting solid is then reused for dye adsorption until saturation is achieved again. This process is repeated five times, and the cyclic efficiency is calculated.

Dynamic Adsorption Experiment of XOF-TIB for Anionic Dyes

XOF-TIB (70 mg) was packed into a chromatography column for the adsorption of organic dye solutions. Aqueous solutions of **MO** (0.04 mM), **EBS** (0.04 mM), and **CR** (0.4 mM) (10 mL each) were pumped through the **XOF-TIB** packed column at a flow rate of 10 mL/min. The UV-Vis spectra before and after adsorption, as well as the color changes of the dye solutions, were recorded.

The percentage of organic dye removal by sample was calculated as:

$Removal\% = 100(C_0 - C_e)/C_0$

where C_0 (mg L^{-1}) is the initial dye concentration; C_e (mg L^{-1}) is the residual dye concentration at equilibrium; V (L) is the volume of dye solution used and m (g) is the mass of adsorbent used.

4. Results and discussion
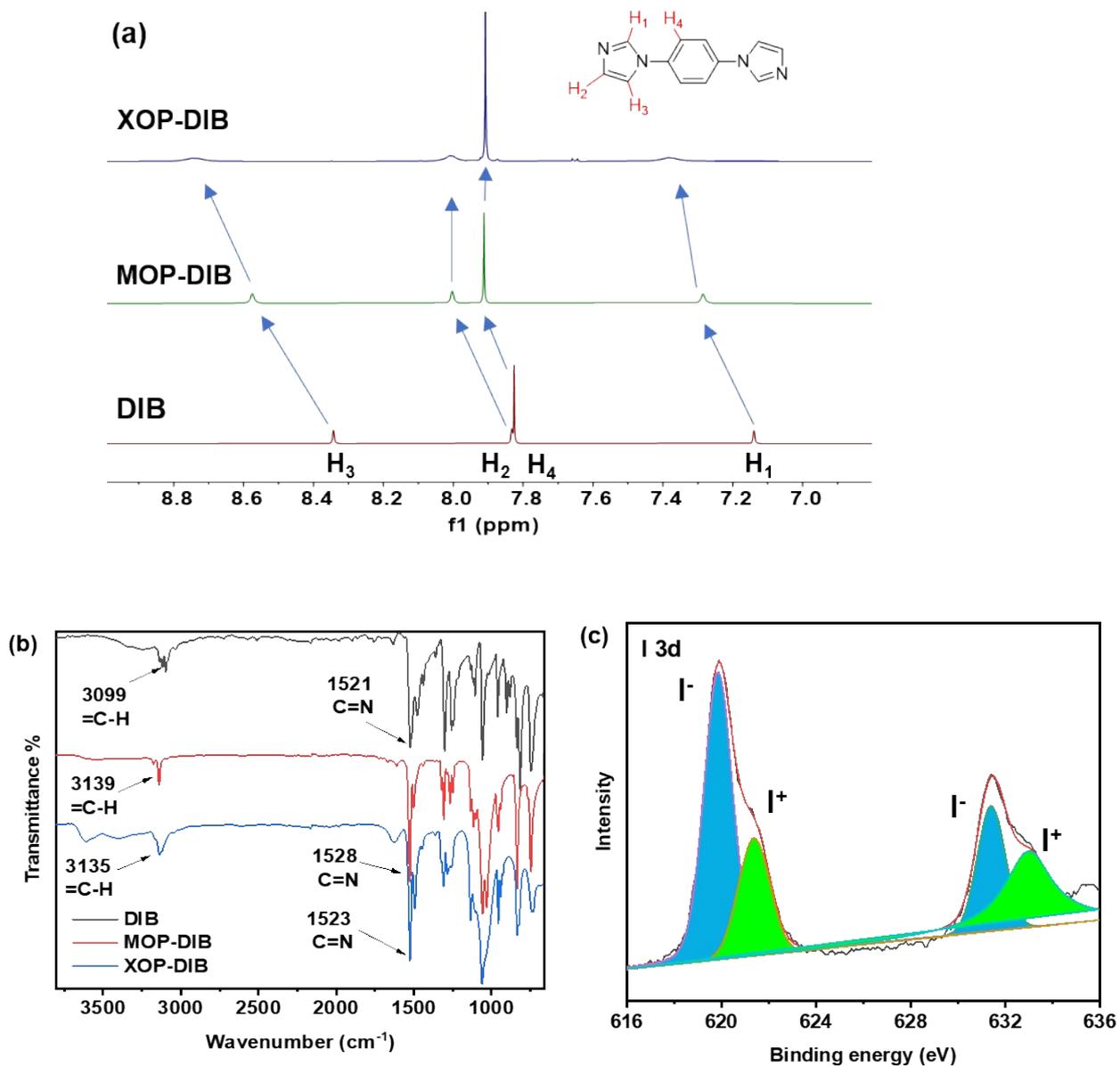
Figure S1. (a) ^{1}H NMR spectra showing the chemical shifts of H_1, H_2, and H_3 protons in **DIB, MOP-DIB,** and **XOP-DIB** in DMSO-d_6. (b) FT-IR spectra of **DIB, MOP-DIB,** and **XOP-DIB** indicating the shifts in =C-H and C=N stretching vibrations. (c) XPS spectrum of I 3d for **XOP-DIB**
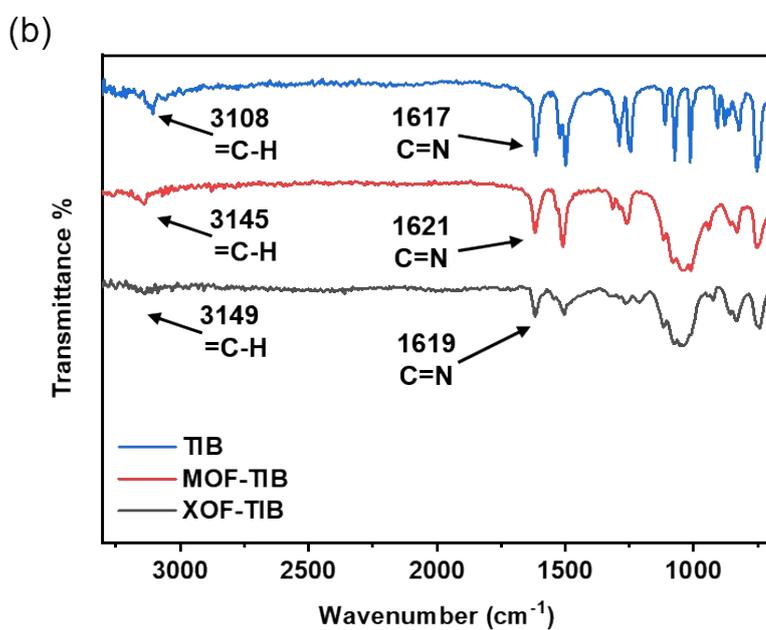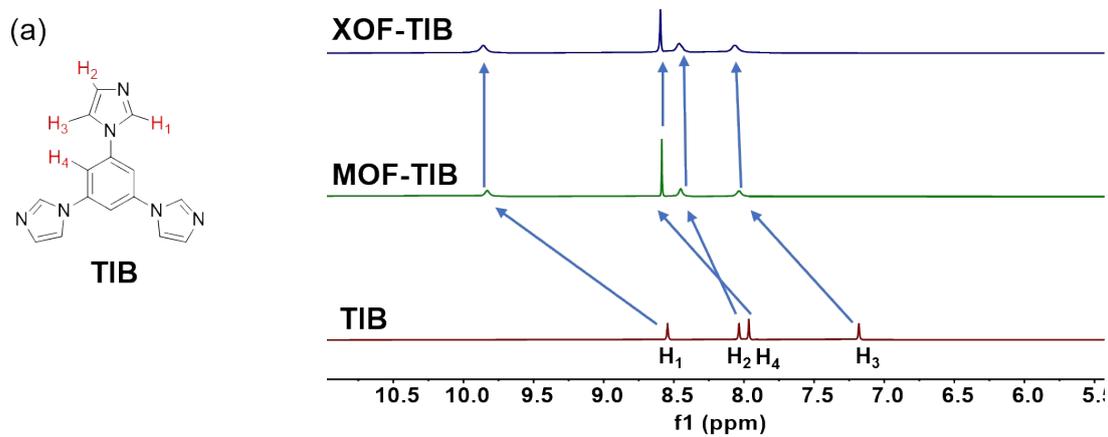
Figure S2. (a) Partial ^{1}H NMR spectra of **TIB**, **MOF-TIB**, and **XOF-TIB** in DMSO-d_6 (600 MHz, 298 K); (b) FT-IR spectra of **TIB**, **MOF-TIB**, and **XOF-TIB**;
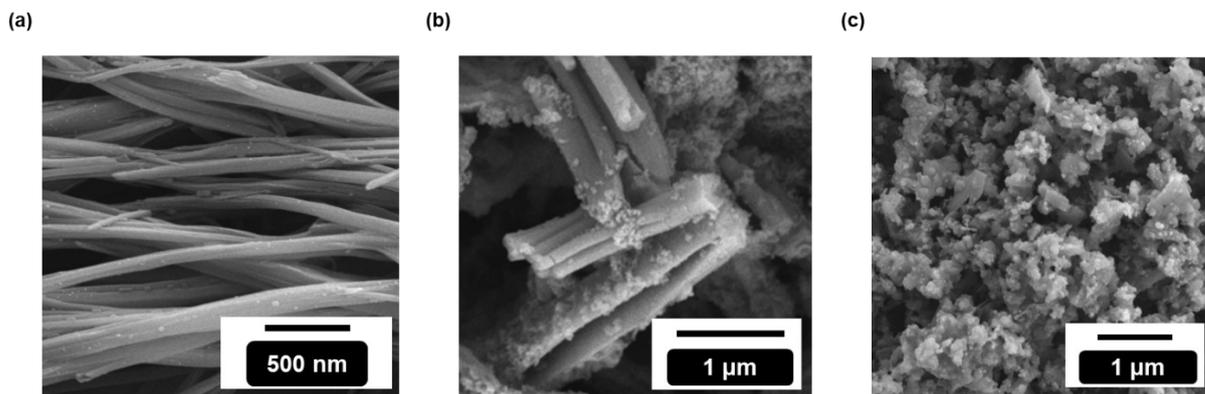
Figure S3. SEM images of (a) **TIB** (b) **MOF-TIB** and (c) **XOF-TIB**
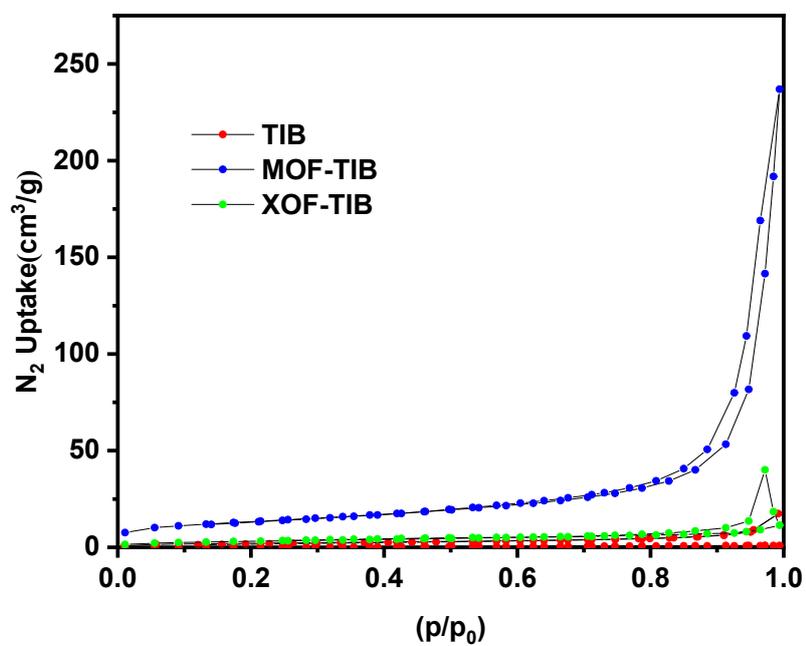
Figure S4. N_2 adsorption isotherm at 77 K for **TIB**, **MOF-TIB**, and **XOF-TIB**.
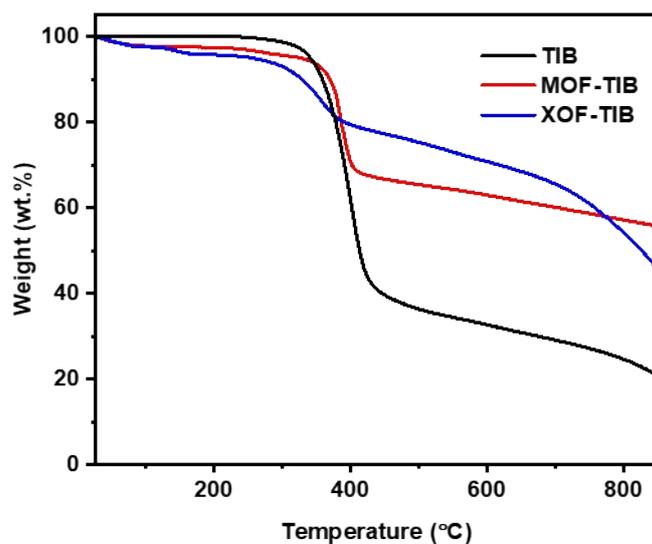
Figure S5. TGA curve of **TIB**, **MOF-TIB**, and **XOF-TIB**.
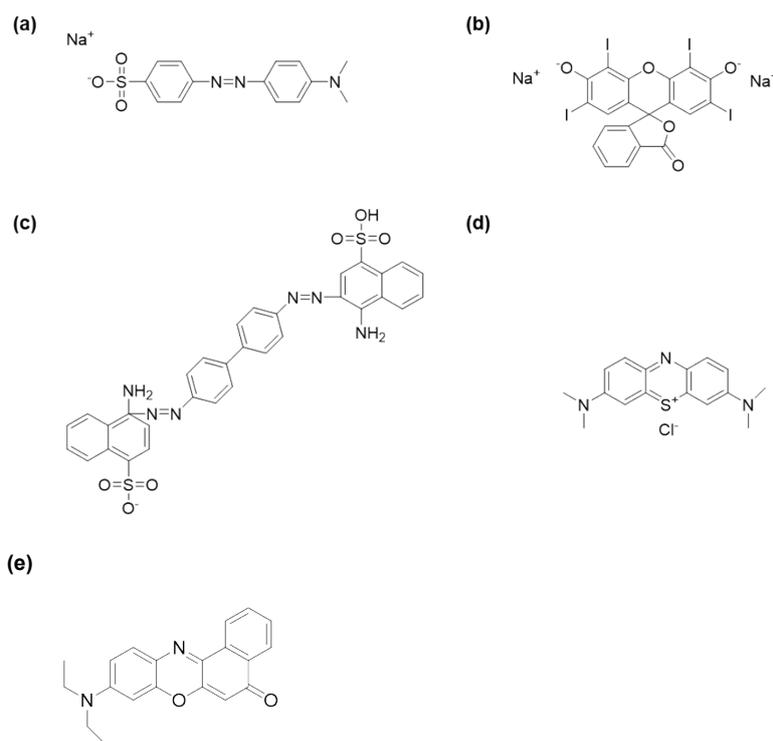
Figure S6. Molecular structures of several cationic and anionic dyes: (a) **MO** (b) **EBS** (c) **CR** (d) **MB** (e) **NR**

(a)
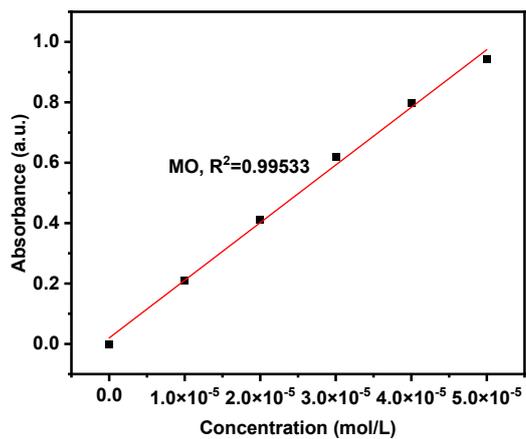
(b)
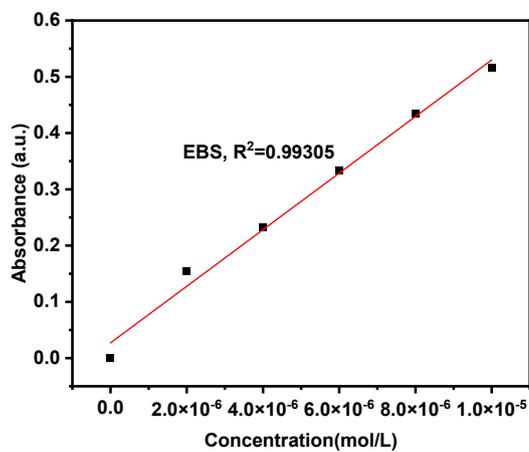
(c)
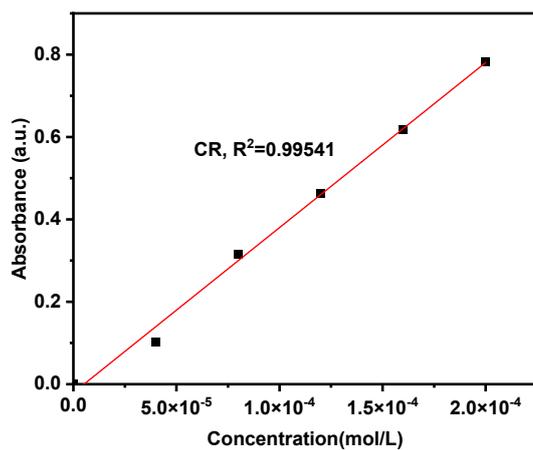
Figure S7. Plots of concentration vs. absorbance intensity of (a) **MO** at 465 nm
(b) **EBS** at 550 nm (c) **CR** at 497 nm
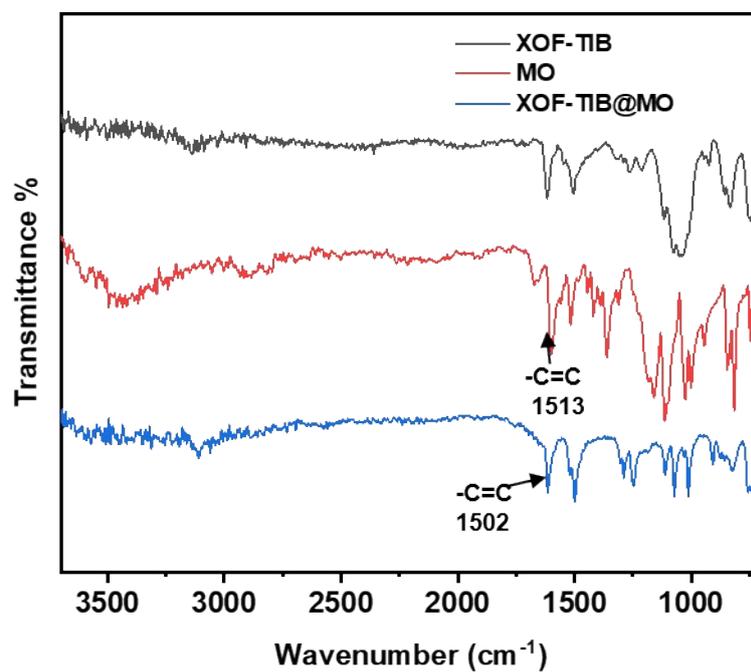
Figure S8. FT-IR spectra of **XOF-TIB** (black), **MO** (red) and **XOF-TIB@MO** (blue)
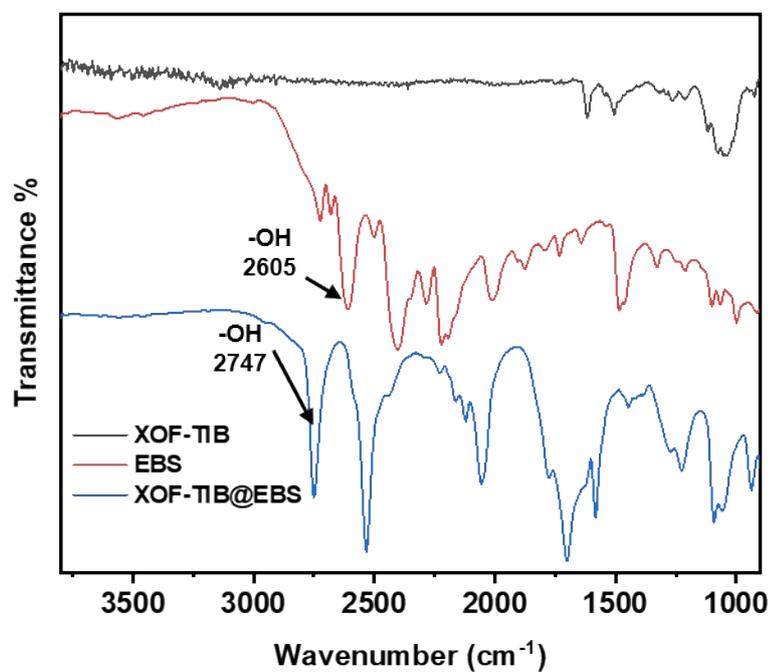
Figure S9. FT-IR spectra of **XOF-TIB** (black), **EBS** (red) and **XOF-TIB@EBS** (blue)
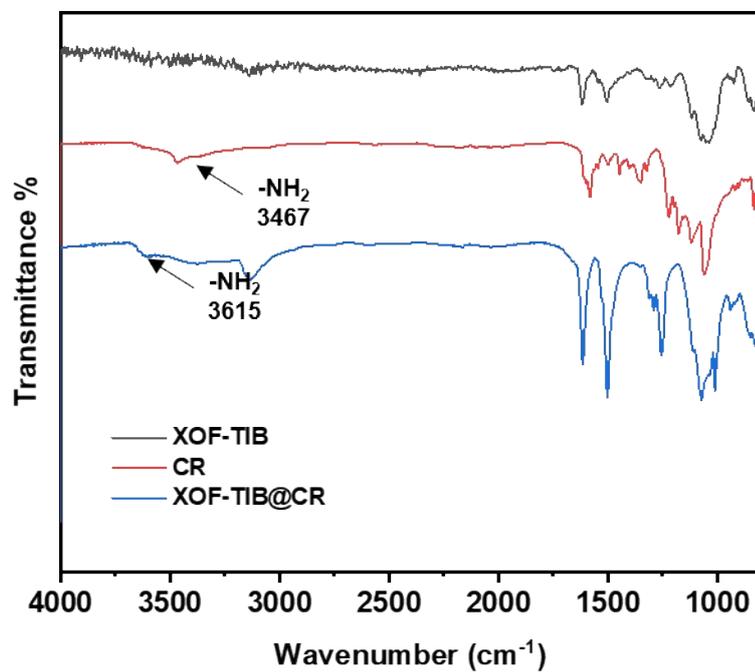
Figure S10. FT-IR spectra of **XOF-TIB** (black), **CR** (red) and **XOF-TIB@CR** (blue)
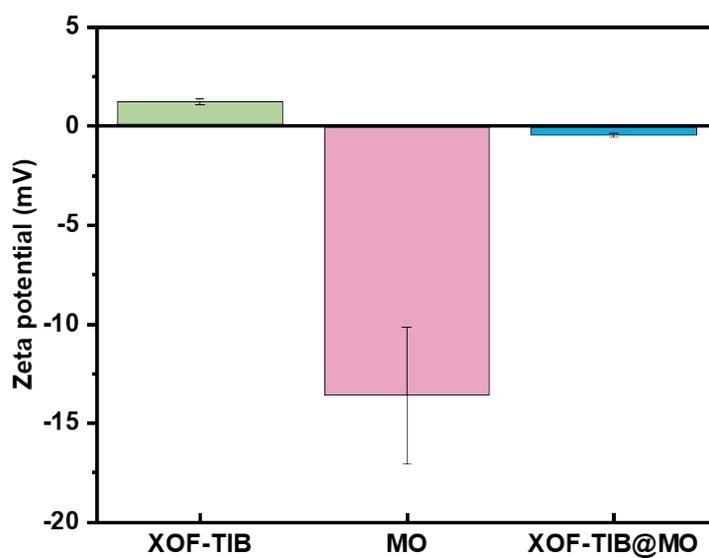
Figure S11. Zeta potenials of **XOF-TIB** (green), **MO** (red) and **XOF-TIB@MO** (blue)
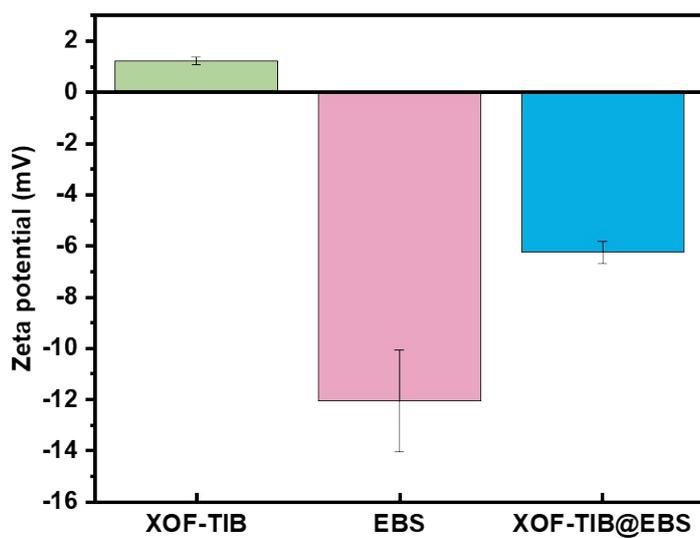
Figure S12. Zeta potenials of **XOF-TIB** (green), **EBS** (red) and **XOF-TIB@EBS** (blue)
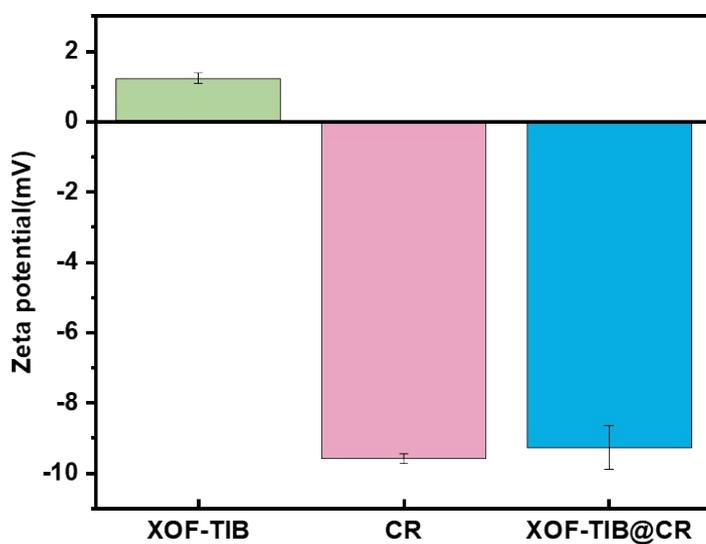
Figure S13. Zeta potenials of **XOF-TIB** (green), **EBS** (red) and **XOF-TIB@CR** (blue)
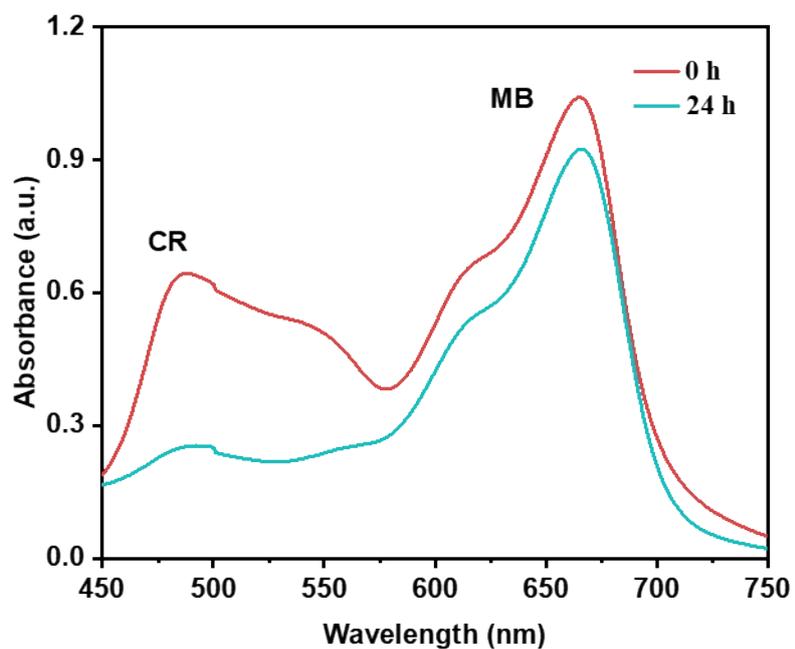
Figure S14. UV-vis selective adsorption spectra of a H_2O solution of dyes (**CR** and **MB**) with **XOF-TIB**

(a)
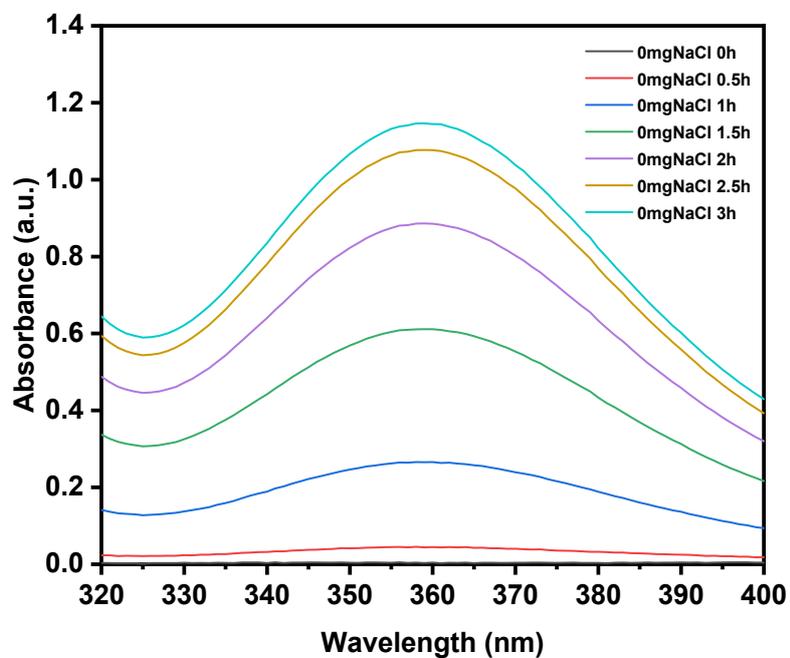
(b)
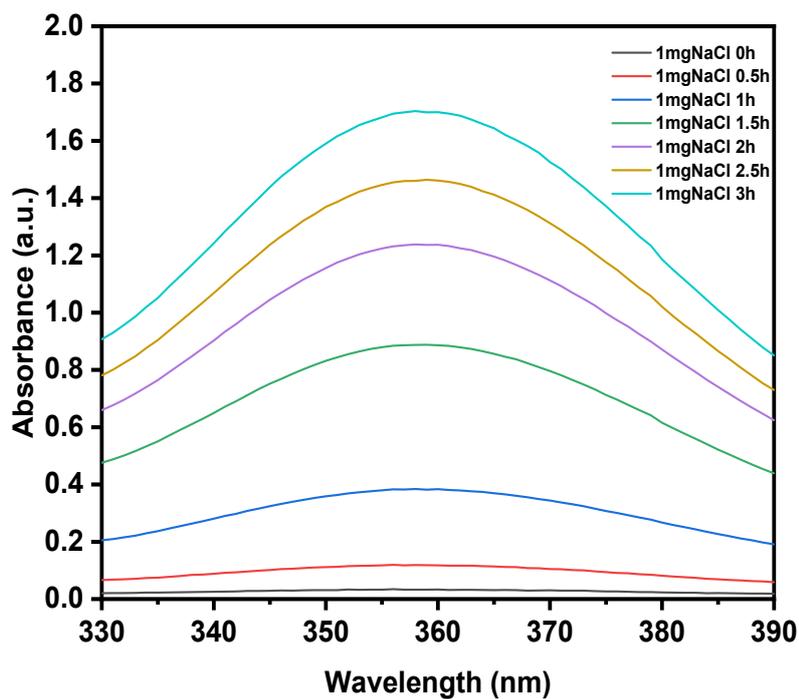
Figure S15. UV−vis desorption spectra of **MO** in ethanol were obtained for **XOF-TIB@MO** under different conditions: (a) without NaCl addition and (b) with NaCl addition.

(a)

(b)

(c)
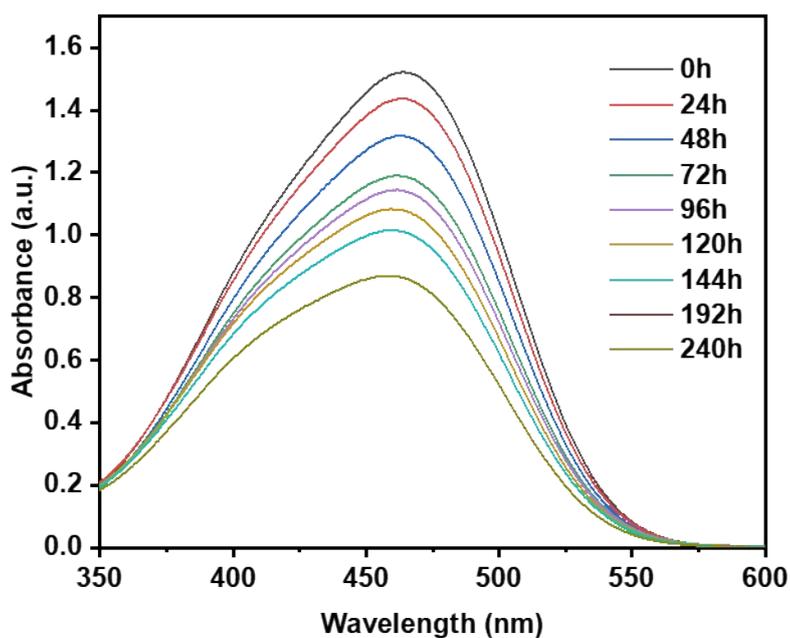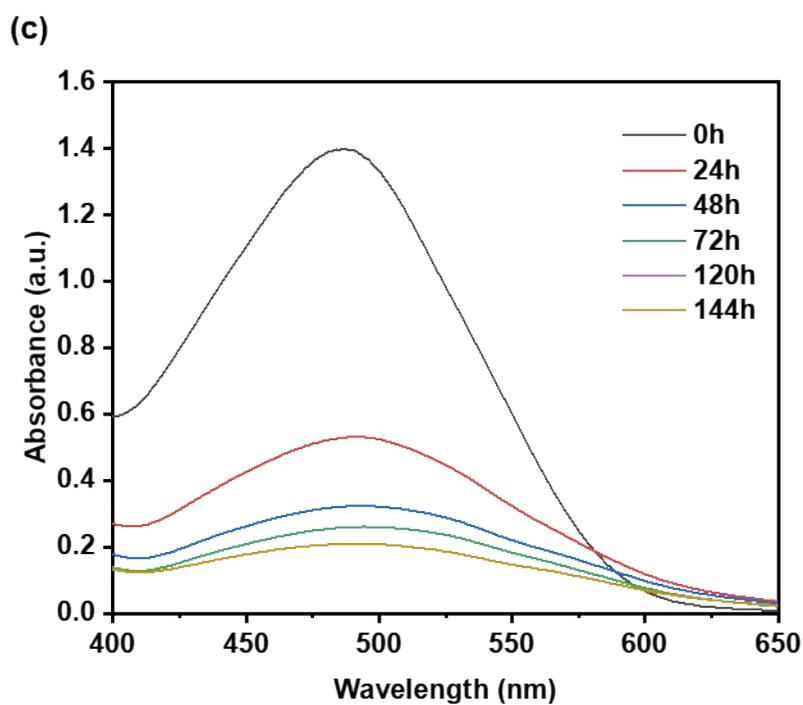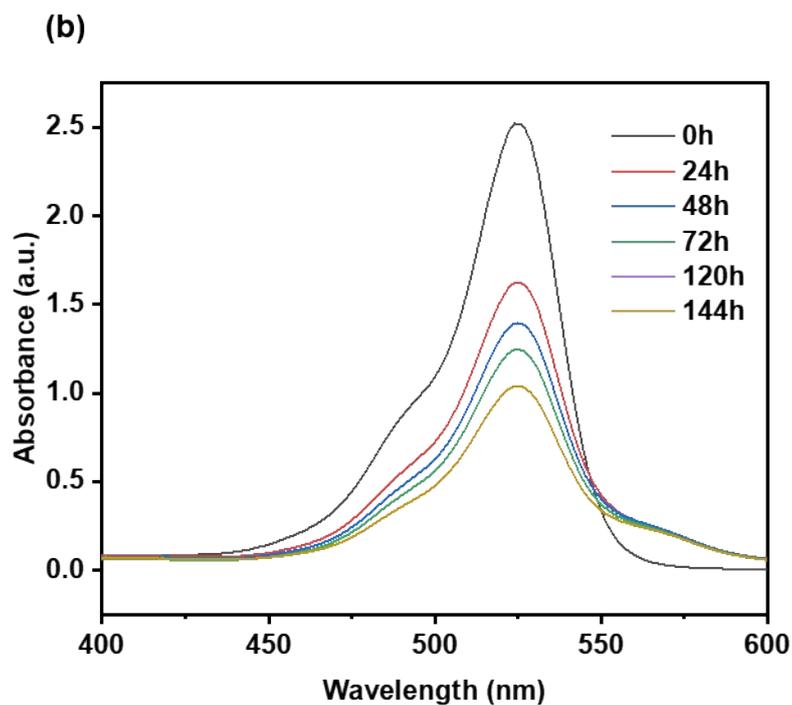
Figure S16. UV-Vis absorption spectra of the maximum adsorption capacity of (a) **MO** (b) **EBS** (c) **CR** on **XOF-TIB**.
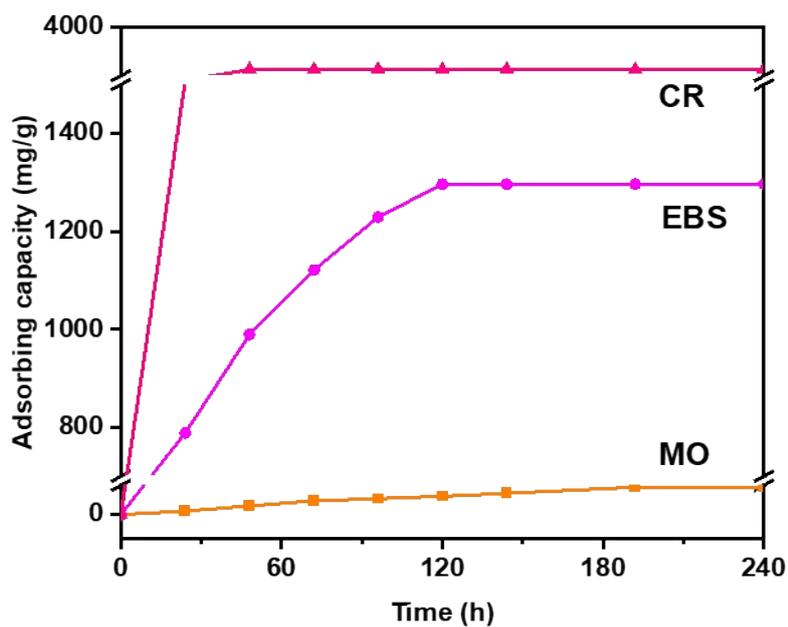
Figure S17. Adsorbing capacity of **MO**,**EBS** and **CR** by **XOF-TIB** as a function of time
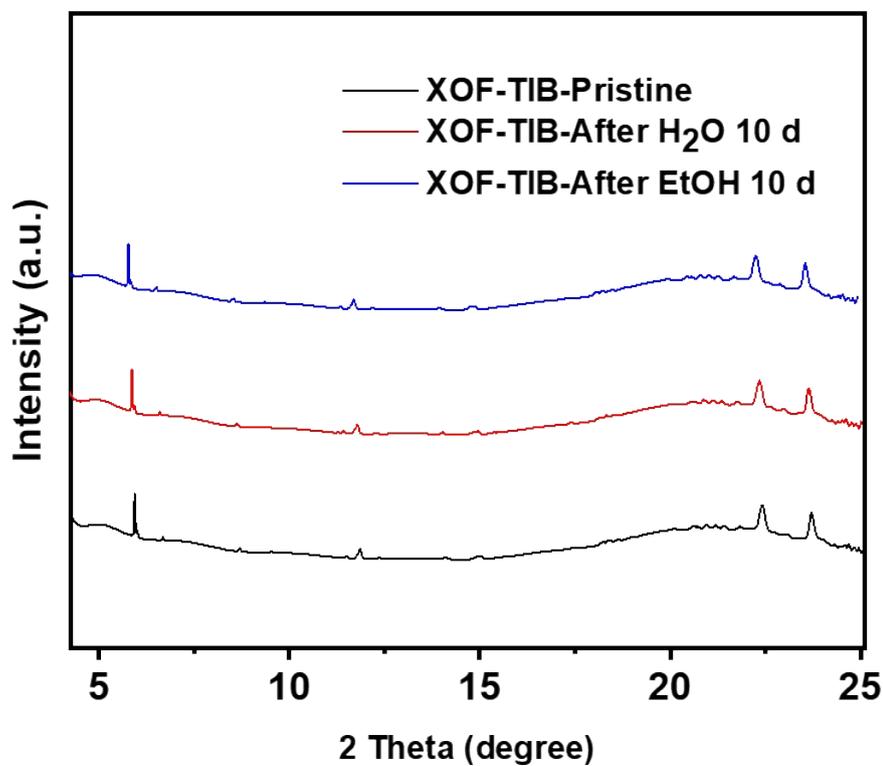
Figure S18. XRD patterns of **XOF-TIB** before and after soaking in water and for 10 days.
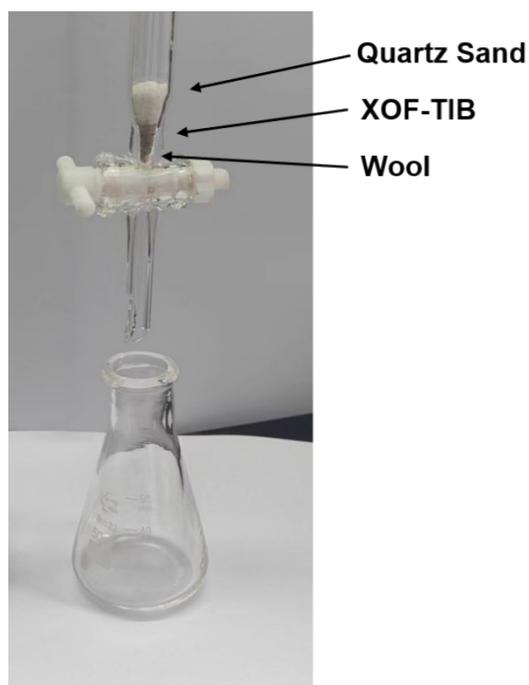
Figure S19. Representation of the **XOF-TIB** (80 mg) loaded column used for column chromatographic separation of dyes in water
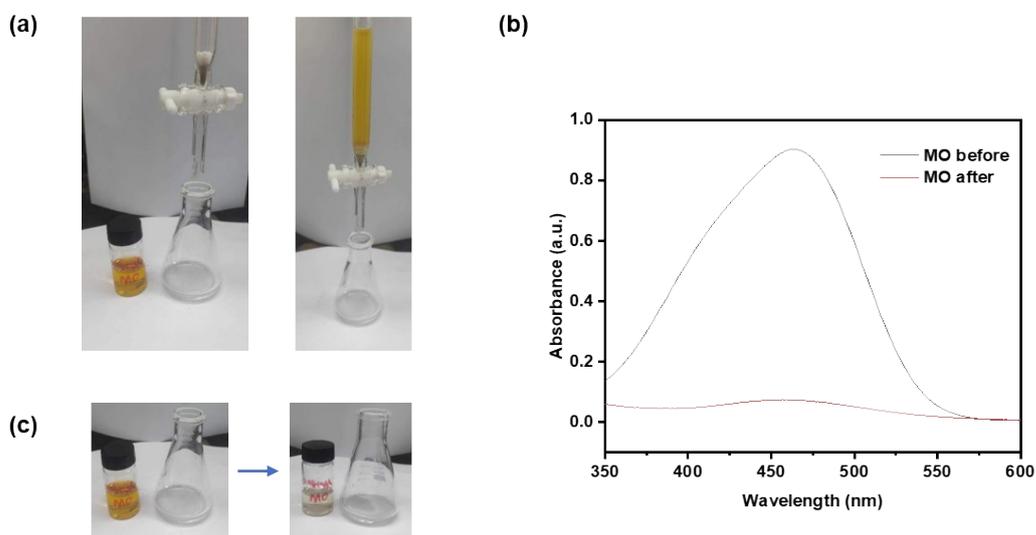
Figure S20. (a) Column chromatography separation of **MO** (0.04 mM) in water using **XOF-TIB** load packed column. (b) Images of **MO** in water before and after passing through the **XOF-TIB** loaded packed column. (c) UV-Vis spectra of **MO** in water before and after passing through the **XOF-TIB** loaded packed column.

(a) (b)

(c)
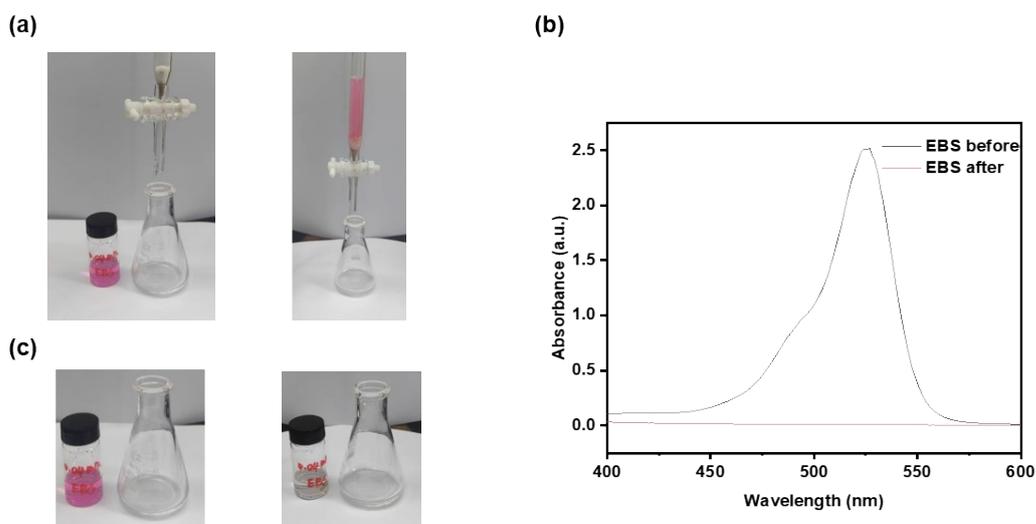
Figure S21. (a) Column chromatography separation of **MO** (0.04 mM) in water using **XOF-TIB** load packed column. (b) Images of **MO** in water before and after passing through the **XOF-TIB** loaded packed column. (c) UV-Vis spectra of **MO** in water before and after passing through the **XOF-TIB** loaded packed column.

(a) (b)

(c)
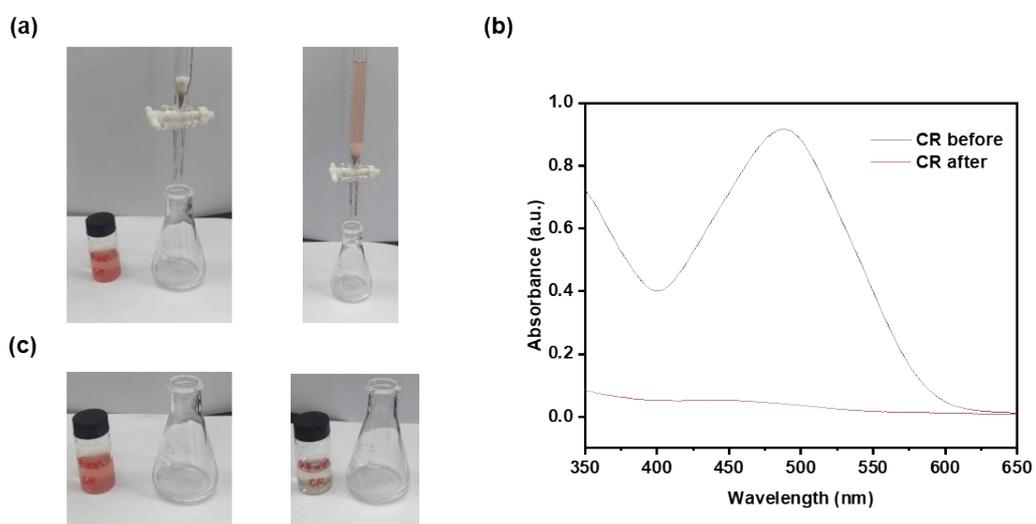
Figure S22. (a) Column chromatography separation of **MO** (0.04 mM) in water using **XOF-TIB** load packed column. (b) Images of **MO** in water before and after passing through the **XOF-TIB** loaded packed column. (c) UV-Vis spectra of **MO** in water before and after passing through the **XOF-TIB** loaded packed column.
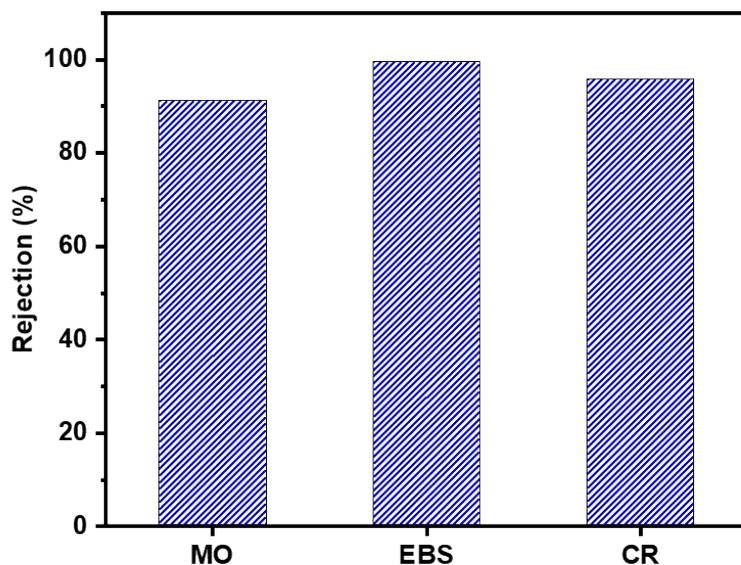
Figure S23. Adsorption rejections of various dyes in **XOF-TIB** load packed column. (**MO**: orange, **EBS**: magenta, **CR**: red)

Table S1. Parameters of the pseudo-first-order and pseudo-second-order kinetic models for the removal of **MO**,**EBS** and **CR** by **XOF-TIB**.

Dyes	C_0 (mol L^{-1})	$q_{e, exp}$ (mg g^{-1})	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
			k_1 (h^{-1})	R_1^2	$q_{e1, cal}$ (mg g^{-1})	k_2 (g mg^{-1} h^{-1})	R_2^2	$q_{e2, cal}$ (mg g^{-1})
MO	4×10^{-5}	2.74	6.95×10^{-3}	0.93998	2.53	3.69×10^{-3}	0.97762	2.82
EBS	4×10^{-5}	10.41	0.26	0.98667	10.02	0.08	0.99008	10.15
CR	4×10^{-4}	78.87	8.68×10^{-3}	0.99515	81.37	1.14×10^{-4}	0.99819	93.94

Table S2. Adsorption equilibrium isotherm models of **XOF-TIB** on **MO**,**EBS** and **CR**.

Isotherm models	Model parameters	MO	EBS	CR
Langmuir	q_m (mg g^{-1})	6.38	177.52	522.50
	K_L (L mg^{-1})	5.9×10^4	1.8×10^3	2.1×10^3
	R^2	0.99357	0.99989	0.99973
Freundlich	K_F ((mg g^{-1}) (L mg^{-1})$^{1/n}$)	6.83×10^3	2.08×10^3	4.24×10^5
	n	1.33	1.02	0.91
	R^2	0.99739	0.99996	0.99994

¹H NMR spectra
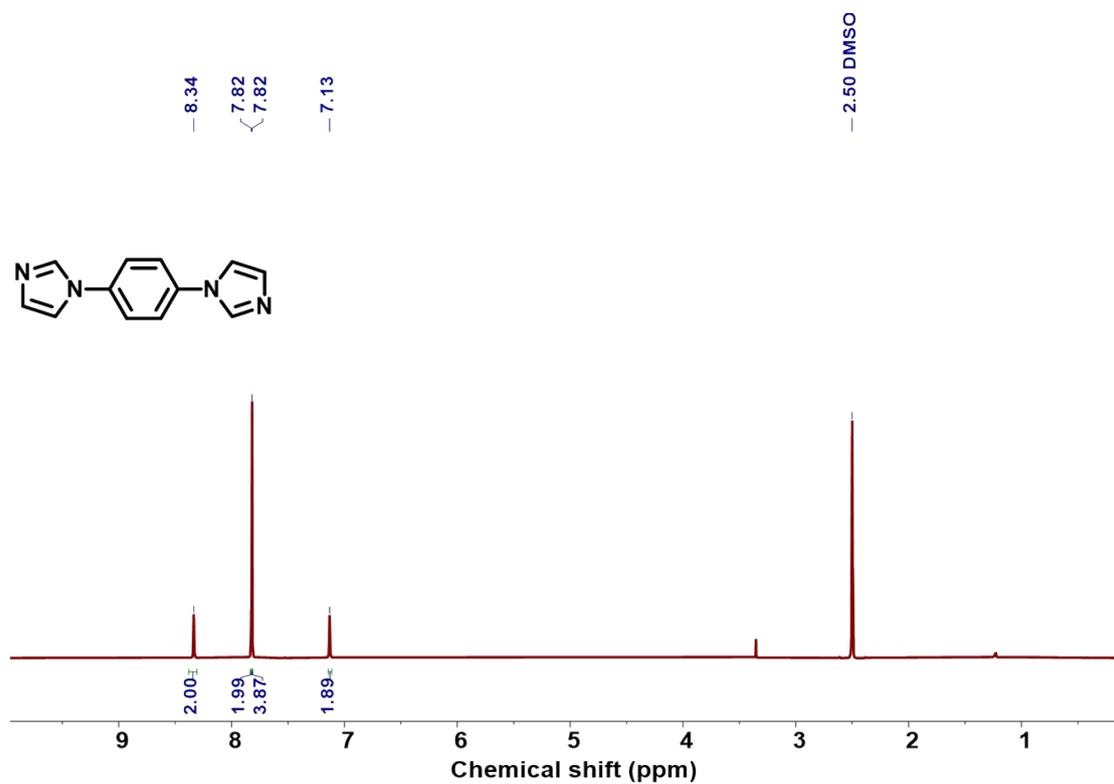
Figure S24. ¹H NMR spectra of **DIB** (DMSO-d_6, 600 MHz, 298 K).
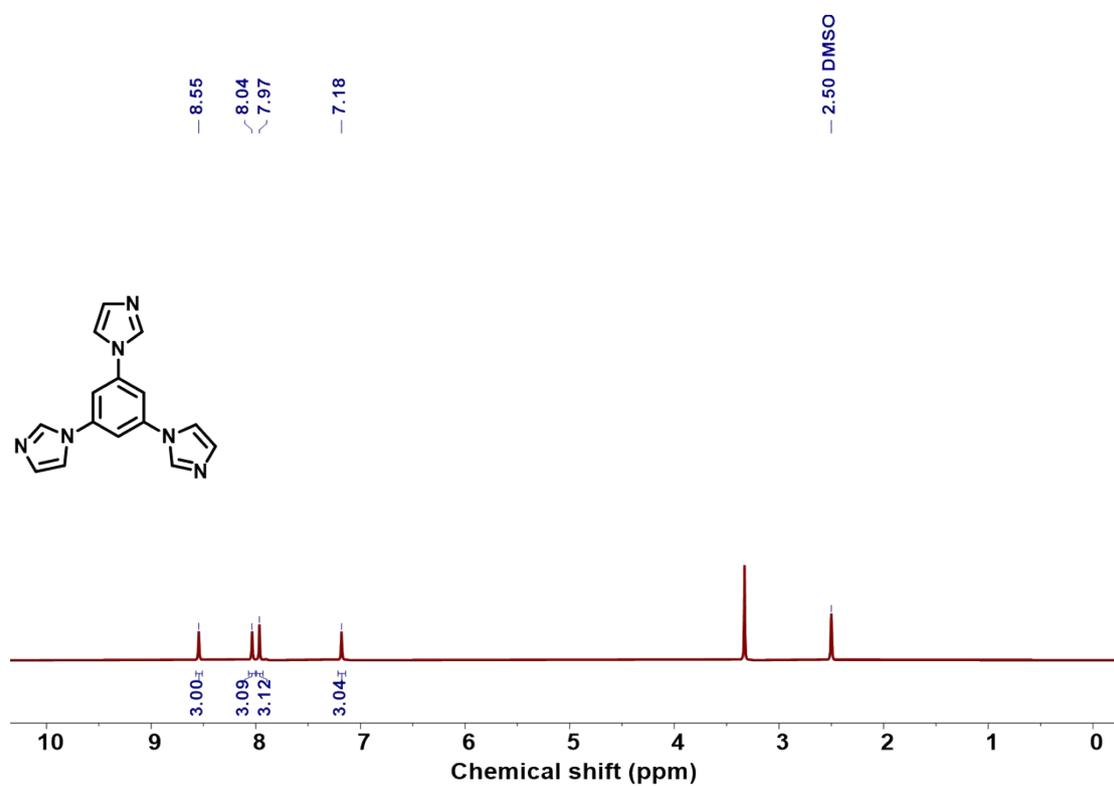
Figure S25. ¹H NMR spectra of **TIB** (DMSO-d_6, 600 MHz, 298 K).