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Supporting Information

Functionalized covalent organic frameworks aerogel for highly efficient removal of anionic and cationic dyes

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I. Preparation of Materials.

Synthesis of mono-(6-amino-6-deoxy)-β-cyclodextrin(6-NH_2-CD):

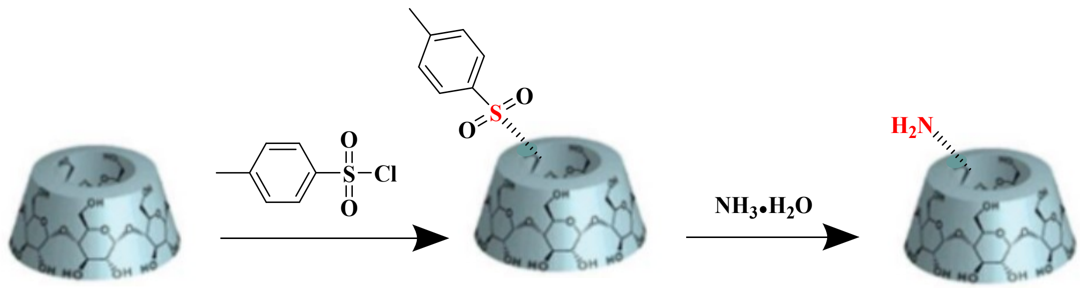
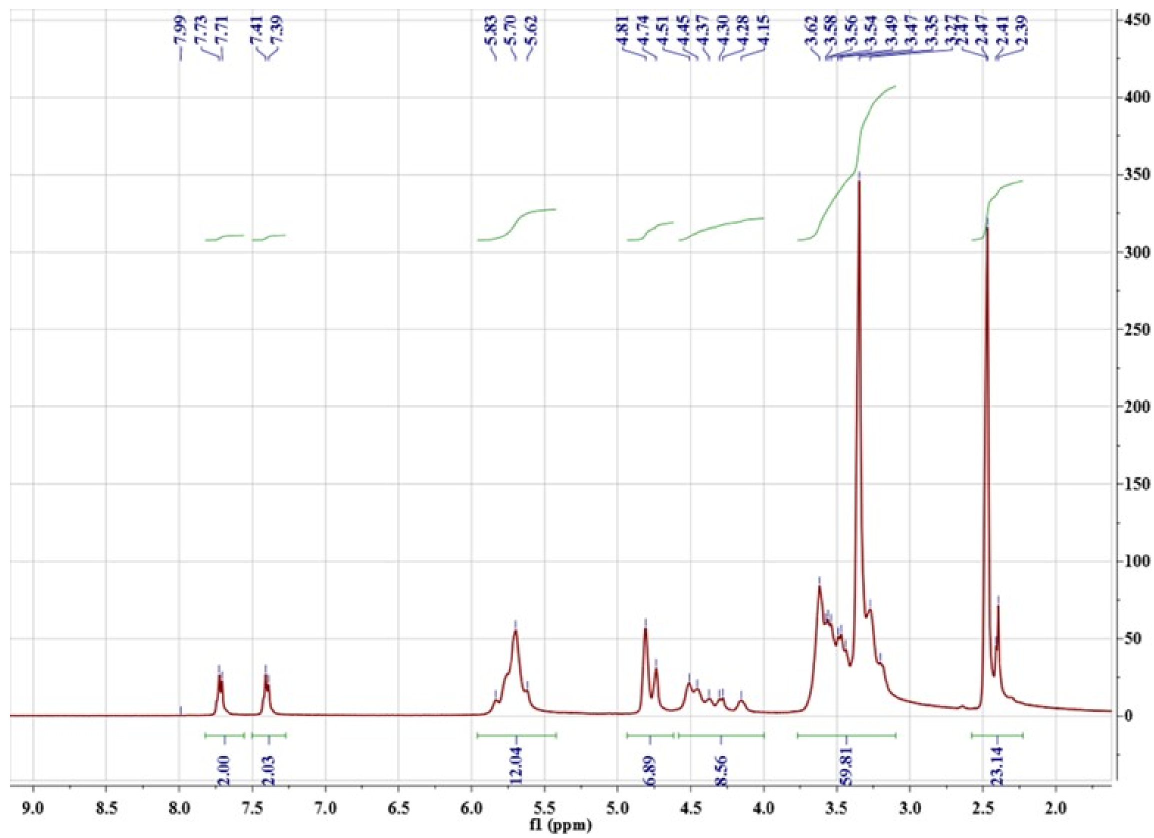


Figure S1 Synthesis of mono-(6-amino-6-deoxy)-β-cyclodextrin(6-NH_2-CD)

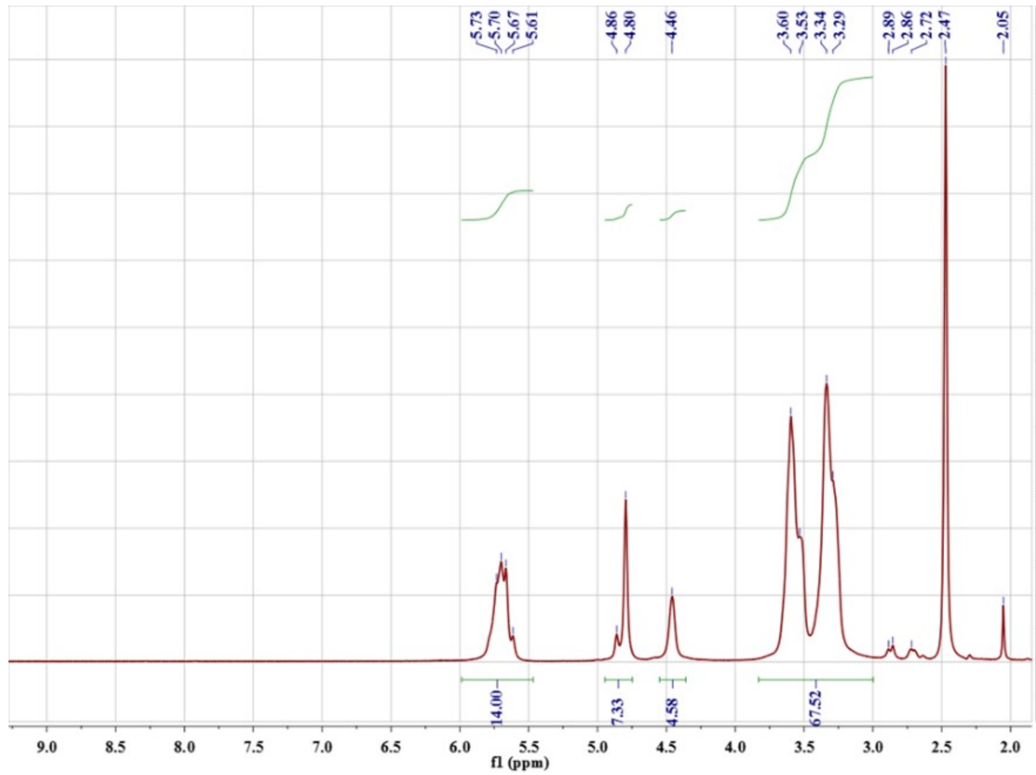
As shown in the image above, mono-6-oxo-p-toluenesulfonyl-β-cyclodextrin(6-CD-OTS) is synthesized first. The product was prepared according to a modified literature synthesi[1]. 6 g (5.28 mmol) of β-cyclodextrin was dispersed in 50 mL of water, stirred vigorously and cooled to below 5 °C in an ice-water bath, then 2 mL of NaOH solution (8.2 M) was added dropwise with a syringe over 4 min. A clear solution was obtained. Next, 874 mg (5 mmol) p-toluenesulfonyl chloride was dissolved in 2 mL CH_3CN and added dropwise to the solution via syringe over 6 min, the reaction mixture was stirred at room temperature for 3 h, and the precipitate was removed by vacuum filtration. The obtained solution was adjusted to pH=7 with 3 M HCl and frozen at 4°C overnight. The precipitate was separated by suction filtration, dissolved in hot water and recrystallized at 4°C for purification. The precipitation was collected by suction filtration. The product was obtained by vacuum drying at 50°C. Yield: 14%

6-NH_2-β-CD(6-NH_2-CD) was prepared as described by Guo et al[2]. 0.64 g 6-OTs-β-CD of powdered was dissolved in 30 mL of ammonia water and stirring at 75 °C for 4 h. After the solution was cooled to room temperature, an appropriate amount of acetone was added to the solution, a large amount of white precipitate was immediately precipitated, then the white precipitate was recovered by suction filtration. The white sedimente was dissolved in mixed solution of H_2O/CH_3OH (v/v=3:1) and precipitated by acetone. This operation was repeated several times to remove the unreacted 6-OTs-β-CD and ammonia. The white precipitate was recovered by suction filtration and dried at 50 °C in vacuum for 24 h. Yield: 17%

II. Supporting figures



FigureS2 1H NMR of mono-6-oxo-p-toluenesulfonyl-β-cyclodextrin



FigureS3 1H NMR of mono-(6-amino-6-deoxy)-β-cyclodextrin

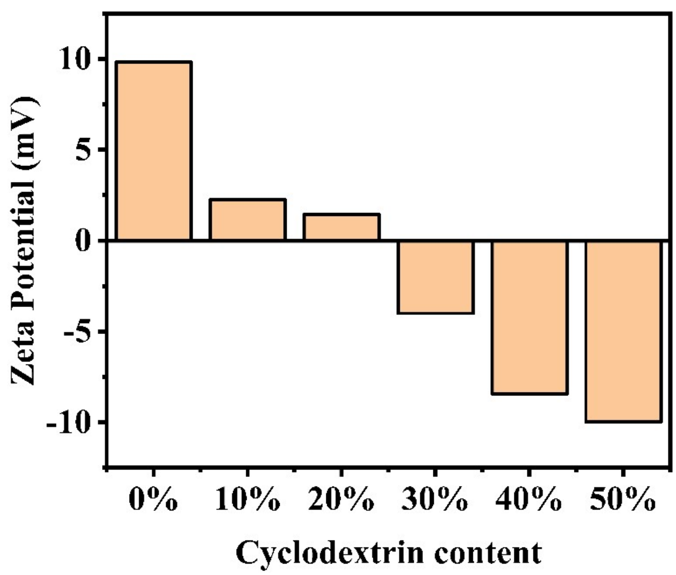


Figure S4 zeta potential of β-CD-TT-COF aerogels with different cyclodextrin contents;

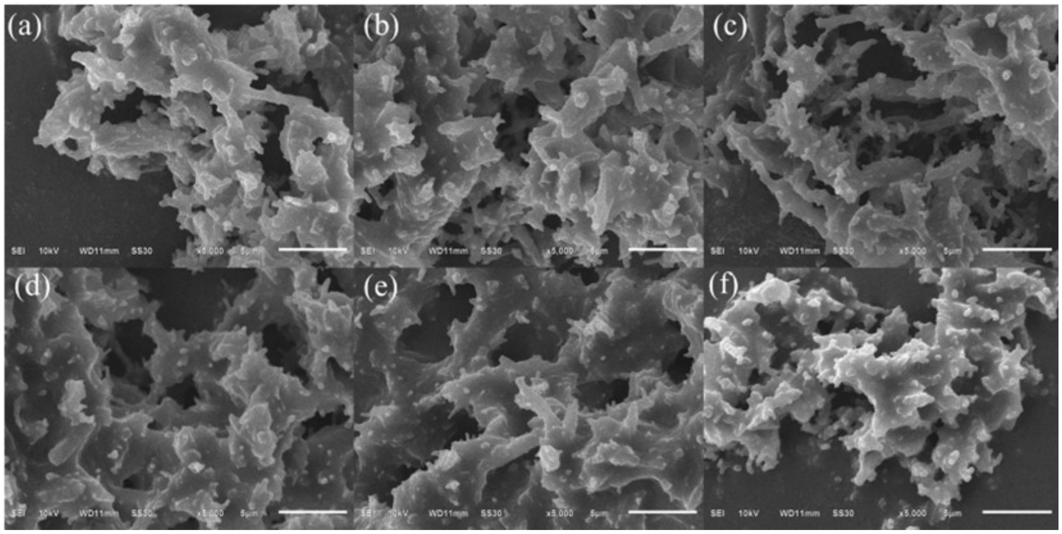


Figure S5 SEM images of β-CD-TT-COF aerogels with different cyclodextrin contents (a) 0%, (b) 10%, (c) 20%, (d) 30%, (e) 40%, (f) 50%

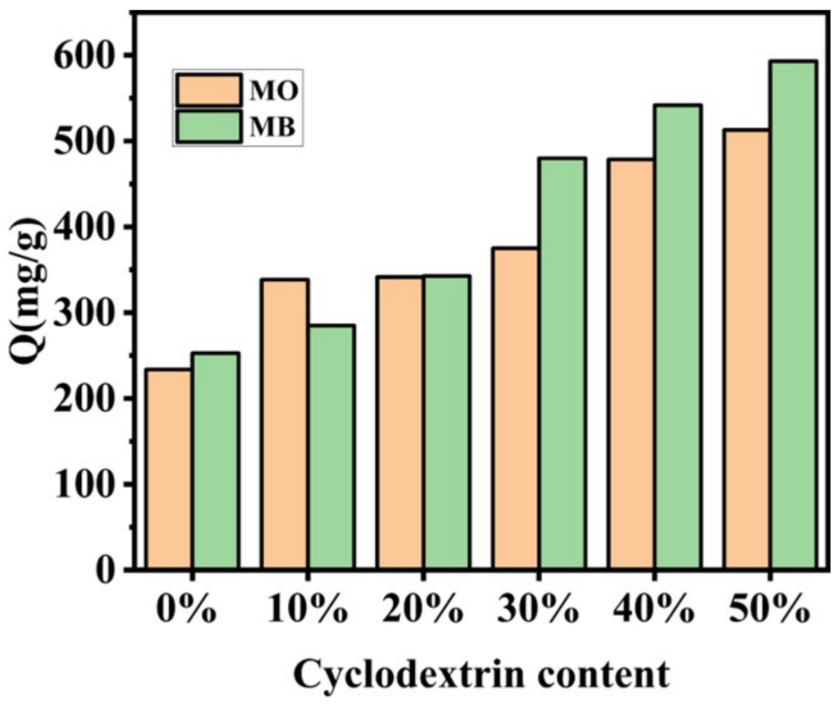


Figure S6 Adsorption capacity (d) of COF aerogels with different 6-NH2-β-CD contents

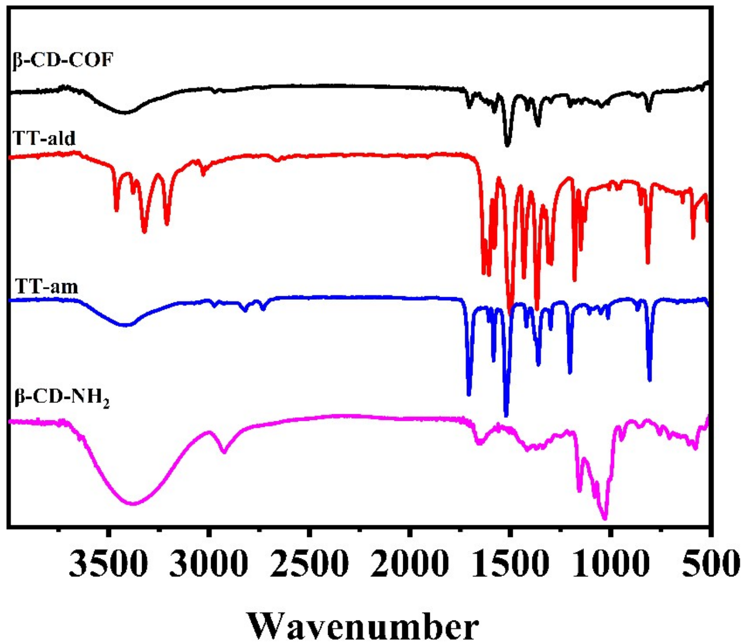


Figure S7 FTIR spectra of β-CD-TT-COF aerogel, aldehyde monomer (TT-ald), amine monomer (TTam) and 6-NH2-β-cyclodextrin;

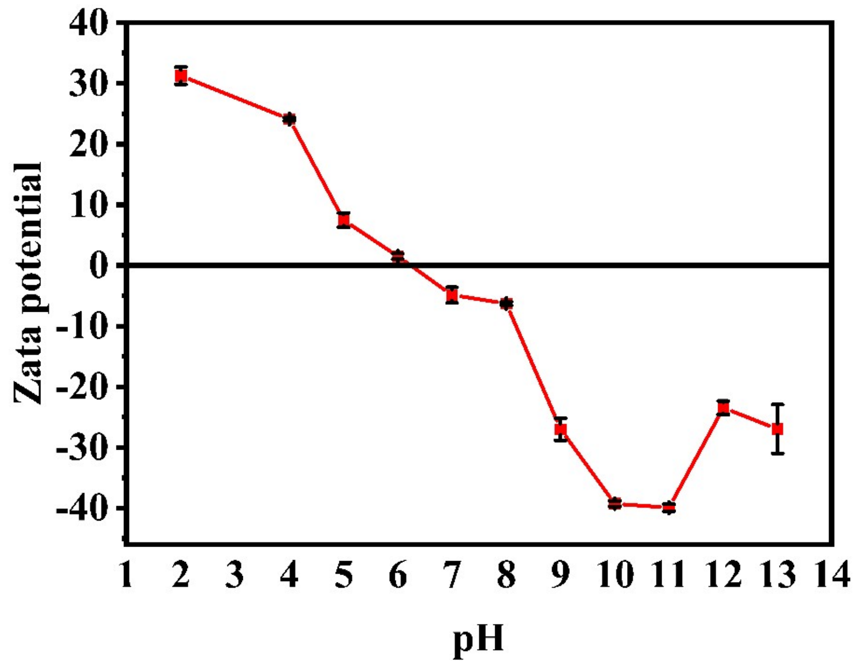


Figure S8 zeta potential of β-CD-TT-COF aerogels with different pH

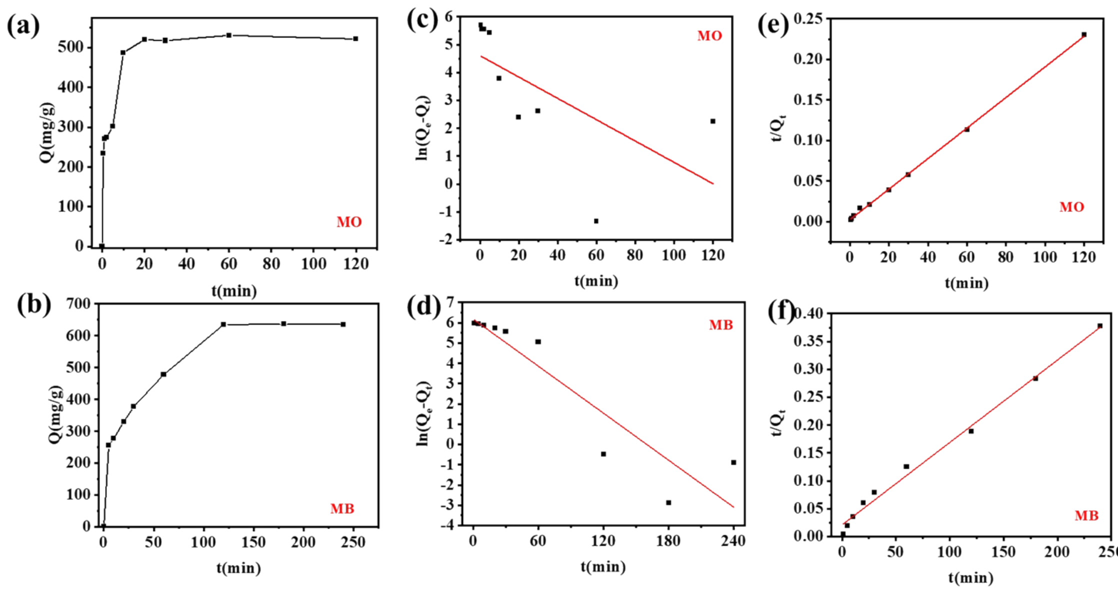


Figure S9 The adsorption kinetic curves (a, b) and pseudo-first-order model (c, d) and pseudo-second-order model (e, f) of β-CD-TT-COF aerogels for methyl orange and methylene blue (dye concentration: 200 mg/ L; sorbent mass: 20 mg, volume: 60 mL, temperature: 310 K)

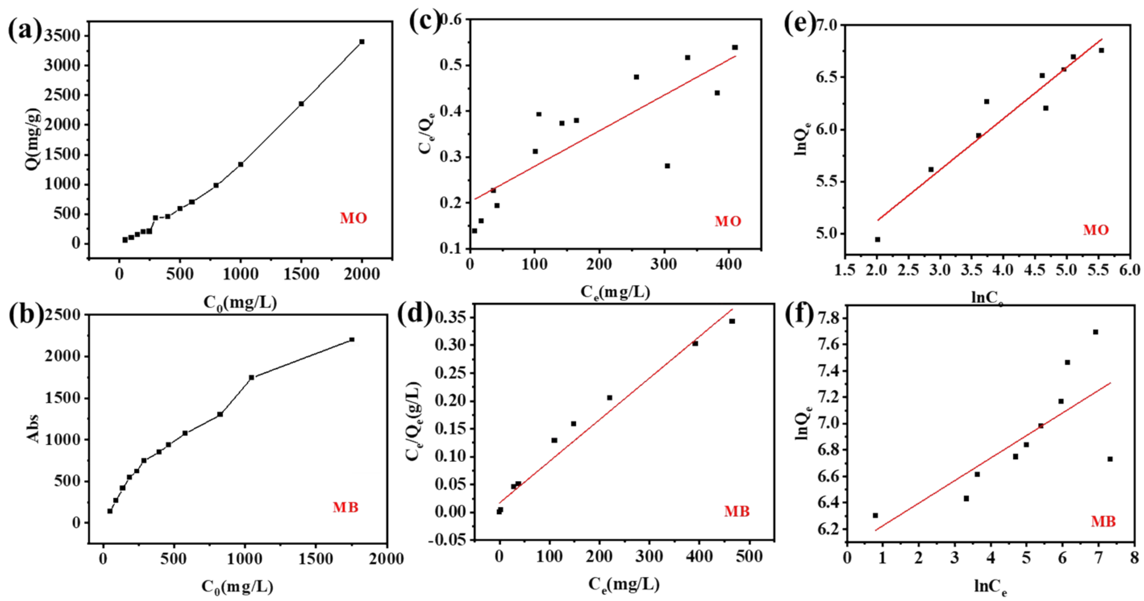


Figure S10 Adsorption isotherms (a, b) and fitting curves of Langumuir model (c, d) and Freundlich model (f, f) of β-CD-TT-COF aerogel for methyl orange and methylene blue (dye concentration: 20-2000 mg/L; adsorption Dosage mass: 2 mg, volume: 6 mL, temperature: 310 K)

III. Supporting tables

Table S1 Molecular sizes and properties of different dyes

Dye molecule	M_W(g/mol)	λ_{max}(nm)	Charge	Molecule size(Å)
Methyl Orange (MO)	327.3	462	-	8.54 × 15.8 × 3.7
Congo Red(CR)	698.7	497	-	26.4 × 7.5× 6.8
Nile Red (NR)	318.4	553	neutral	14.2 × 6.5 × 3.1
Calcein（CA）	622.5	369	neutral	12.2× 7.5 × 7.7
Methylene Blue(MB)	319.9	553	+	13.4 × 5.0 × 4.2
Rhodamine B(RhB)	479.0	664	+	15. 9 × 12.0 × 5.6

Table S2 Synthesis ratio of β-CD-COF aerogels with different defect contents

	TT-ald(mg)	TT-am(mg)	β-CD-NH_2(mg)	β-CD-NH_2 contains NH_2 for all NH_2 content	Yield(mg)
①	23.6 (0.06 mmol)	21.3 (0.06 mmol)	0	0	45
②	23.6 (0.06 mmol)	19.3 (0.054 mmol)	6.8 (0.006 mmol)	10 %	42.6
③	23.6 (0.06 mmol)	17.0 (0.048 mmol)	13.6 (0.012 mmol)	20 %	35.4
④	23.6 (0.06 mmol)	14.9 (0.42 mmol)	20.41 (0.018 mmol)	30 %	33.7
⑤	23.6 (0.06 mmol)	12.8 (0.036 mmol)	27.21 (0.024 mmol)	40 %	28.5
⑥	23.6 (0.06 mmol)	10.6 (0.03 mmol)	34.02 (0.03 mmol)	50 %	24.6
⑦	23.6 (0.06 mmol)	8.43 (0.03 mmol)	40.82 (0.03 mmol)	60 %	15.8

Table S3 The comparison of adsorption performance of β-CD-COF aerogel and other adsorbents for MO and MB.

Adsorbent	Dye	Adsorption capacity/($mg \cdot g^{-1}$)	Reference
Benzodiimidazole-COF	MO	256.0	[3]
Benzodiimidazole-COF	MB	185.0	[3]
MOF-235	MO	477	[4]
MOF-235	MB	187	[4]
TS–COF–1	MB	1691	[5]
TPT-DMBD-COF	MB	45.45	[6]
ICOFs	MO	290.0	[7]
GA10 aerogel	MO	16	[8]
GO-CS aerogels	MO	543.4	[9]
GO-CS aerogels	MB	110.9	[9]
Graphene aerogel	MO	419	[10]
3D rGO/ZIF-67 aerogel	MO	350	[11]
β-CD-COF aerogels	MO	3403.91	This work
β-CD-COF aerogels	MB	2199.37	This work

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