Supporting Information

Novel Three-dimensional Fibrous Covalent Organic Framework Constructed via Silver Amalgam Bridging for Efficient Organic Dye Adsorption and Removal

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1. Materials and Instruments. 1,3,6,8-tetrakis(4-formyl phenyl)pyrene (TFP), 4,4'-(1,10-phenanthroline-2,9-diyl)dianiline (PDA) tertbutyl (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)carbamate, 2,9-Dibromo-1,10-phenanthroline, 1,3,6,8-tetrabromopyrene, 4-formylphenylboronic acid were purchased from Bide Pharmatech Ltd. (Shanghai, China). Acetone, tetrahydrofuran (THF), 1,4-dioxane, potassium carbonate, o-dichlorobenzene (o-DCB), n-butanol (n-BuOH), acetic acid (HAc), ethanol (EtOH), sodium acetate, silver nitrate ($AgNO_3$), mercuric nitrate ($Hg(NO_3)_2$), methylene blue (MB), methyl orange (MO), Rhodamine B (RhB) and Eriochrome Black T (EBT) and other reagents were purchased from Aladdin Industrial Inc. (Shanghai, China). Tap water, Lake water and river water were obtained from the Chemistry build of Northeastern University, Nanhu Park and Hunhe River, respectively. Deionized water was prepared from the Millipore system. All reagents were analytical grade and used without further purification.

Powder X-ray diffraction (PXRD) patterns were collected on a Maxima XRD-7000 diffractometer (Shimadzu, Japan). N_2 adsorption-desorption isotherms were calculated by an Autosorb-IQ-MP-C automatic gas adsorption analyzer at 77 K (Quantachrome, USA). Thermogravimetric analysis (TGA) was determined using a TGA/DSC 3+ thermogravimetric analyzer (Mettler Toledo, Switzerland) under a nitrogen atmosphere at a heating rate of 10 min^{-1}. Scanning electron microscopy (SEM) images were collected on a SU8010 field-emission electron microscope at a voltage of 5.0 kV (Hitachi, Japan). Transmission electron microscopy (TEM) images are recorded on a Tecnai G220 microscope (Philips, Holland). Fourier transform infrared

(FT-IR) spectra were recorded using a Nicolet-6700 FT-IR spectrophotometer (Thermo Scientific, USA). Ultra-violet-visible (UV-vis) absorption spectra were obtained on a U-3900 UV-vis spectrophotometer (Hitachi, Japan).

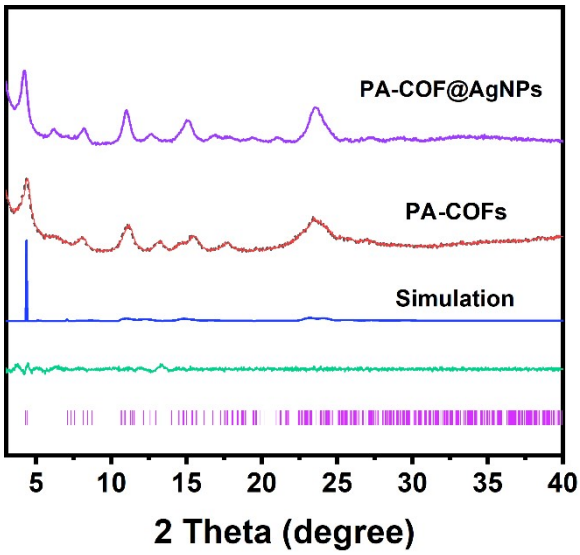


Fig. S1. XRD patterns of PA-COF: experimental data (red), Pawley refinement (black), difference between experimental and refined values (green), Bragg position (pink), simulated AA stacking mode (blue), XRD pattern of PA-COF@AgNPs (purple).

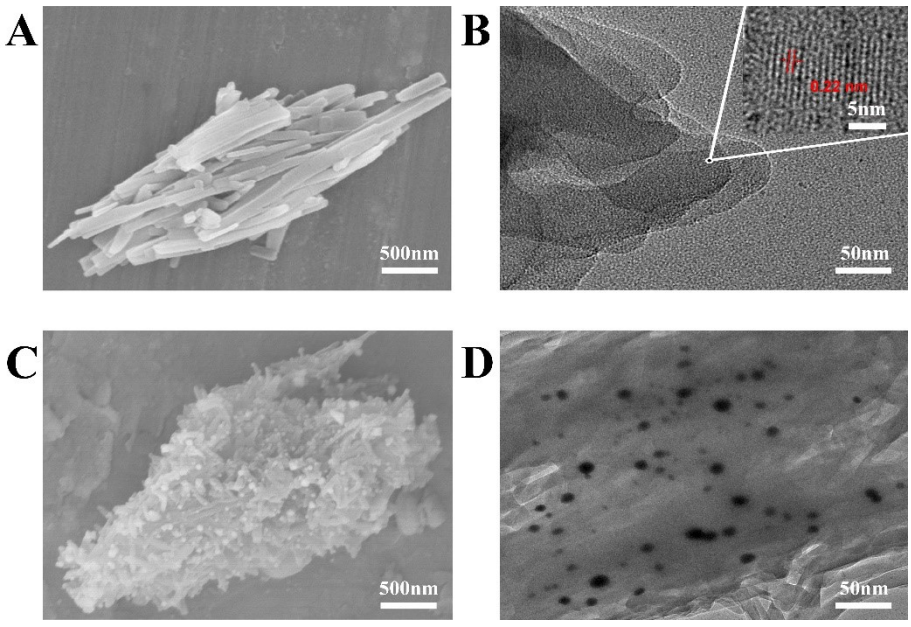


Fig. S2. SEM (A) and TEM (B) image of PA-COF, inset: High-resolution TEM image of PA-COF. SEM (C) and TEM (D) image of PA-COF@AgNPs composite.

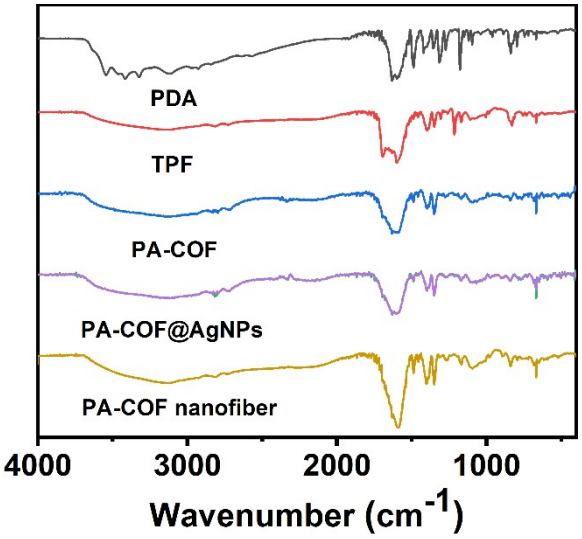


Fig. S3. FT-IR spectra of PDA, TFP, PA-COF, PA-COF@AgNPs and PA-COF nanofiber.

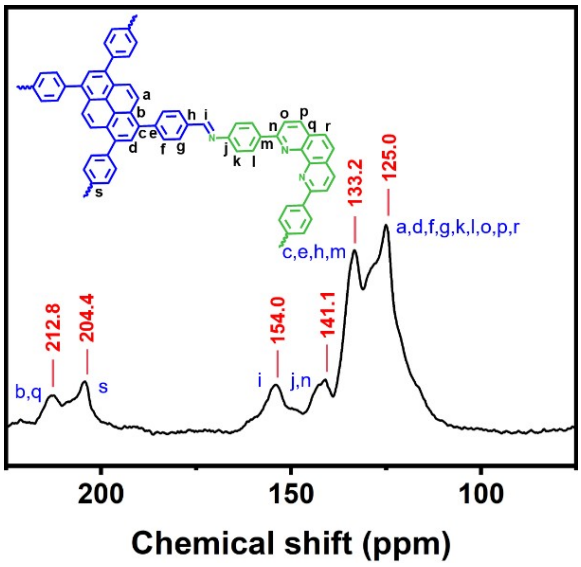


Fig. S4. Solid-state ^{13}C CP-MAS NMR spectrum of PA-COF nanofiber.

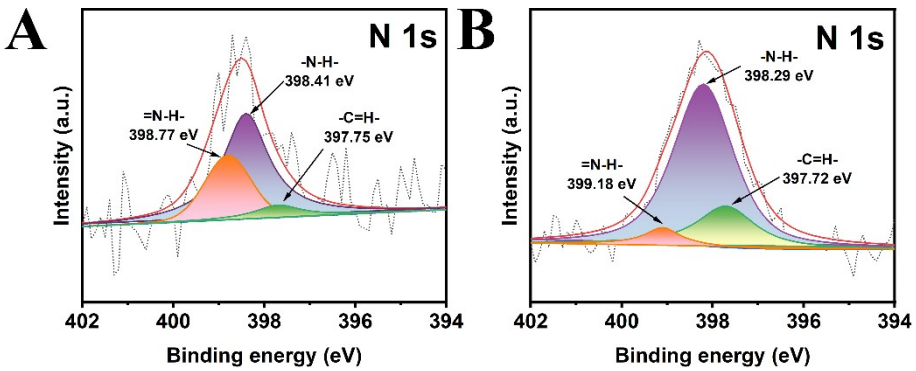


Fig. S5. High-resolution XPS spectra of N 1s of (A) PA-COF and (B) PA-COF@AgNPs.

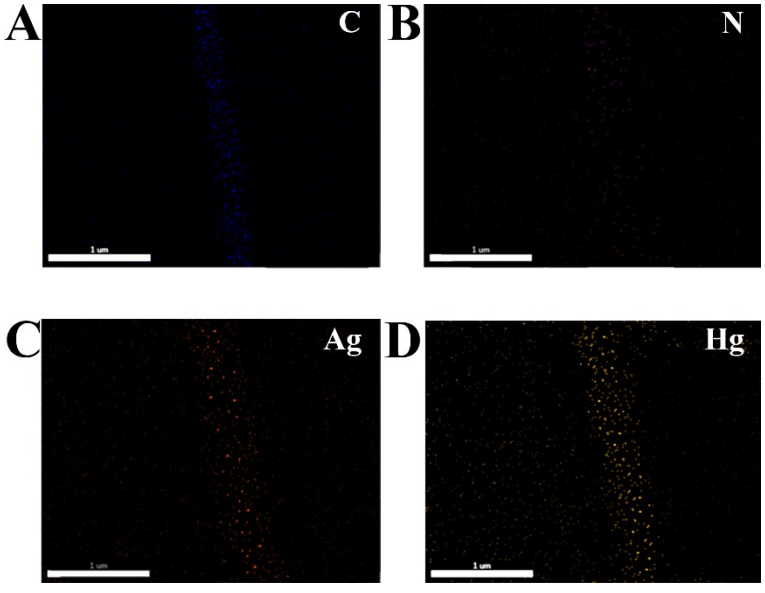


Fig. S6. EDS mapping of PA-COFs nanofiber.

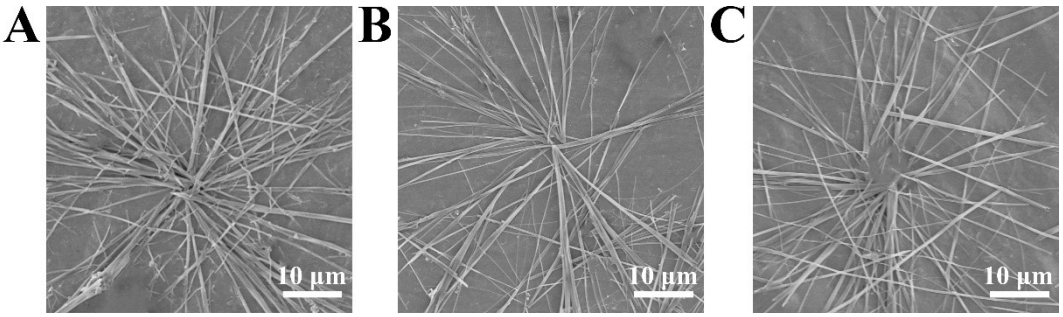


Fig. S7. SEM images of PA-COF nanofiber prepared from different batches.

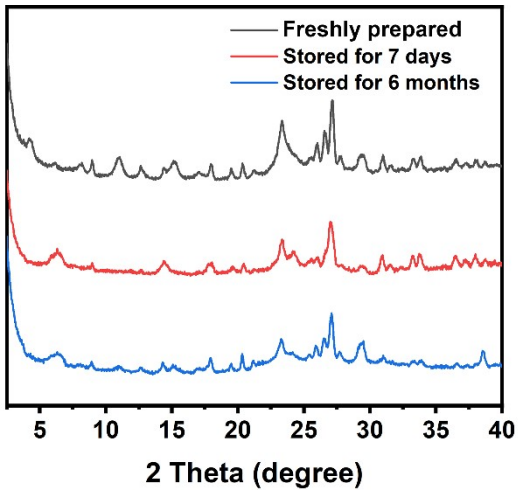


Fig. S8. XRD patter of PA-COF nanofiber: freshly prepared, stored for 7 days and 6 months.

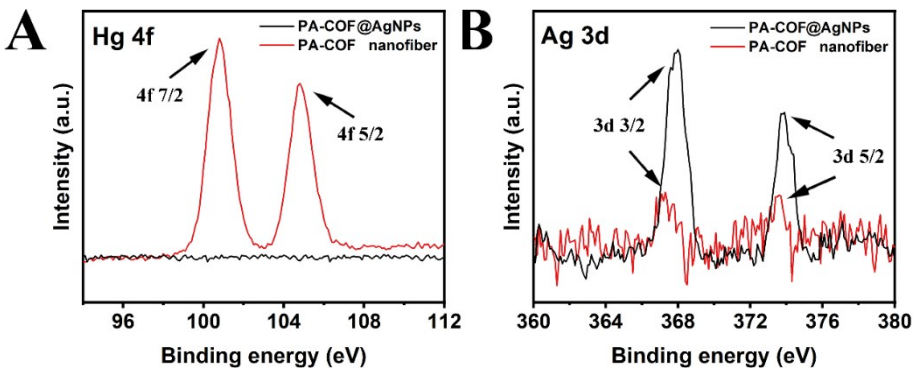


Fig. S9. High-resolution XPS spectra of (A) Hg 4f and (B) Ag 3d of PA-COF@AgNPs and PA-COF nanofiber.

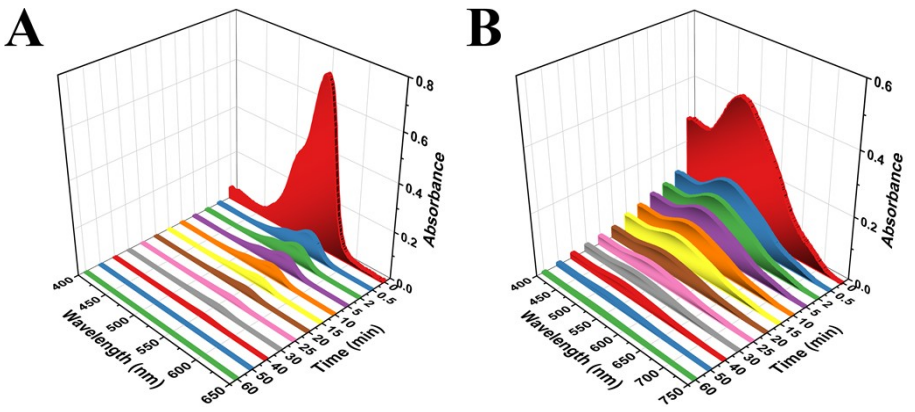


Fig. S10. Time-dependent UV-Vis spectra of (A) RhB (c_0 = 50 mg L^{-1}) and (B) EBT (c_0 = 50 mg L^{-1}) treated with PA-COF nanofiber.

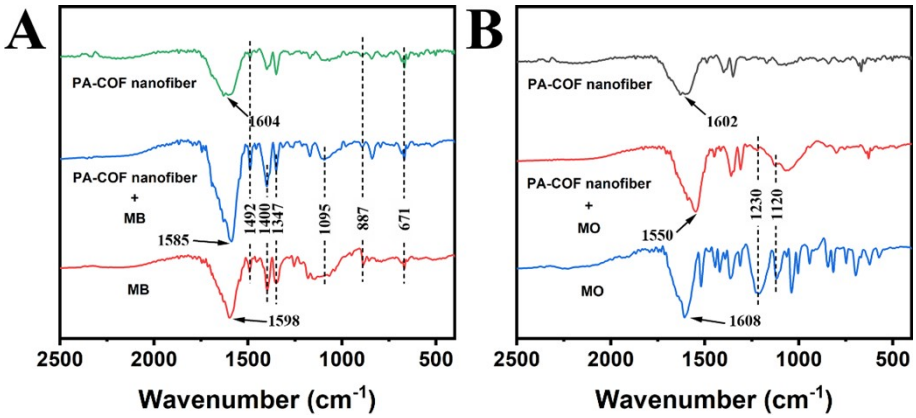


Fig. S11. FTIR spectra of (A) PA-COF nanofiber, MB and PA-COF nanofiber@MB, (B) PA-COF nanofiber, MO and PA-COF nanofiber@MO.

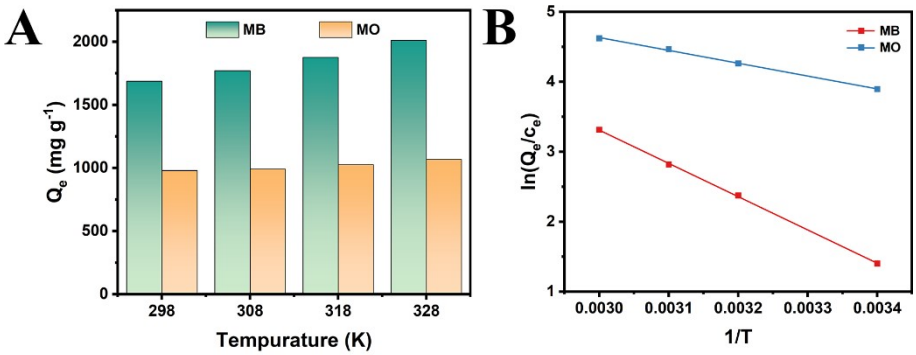


Fig. S12. (A) Adsorption capacities of PA-COF nanofiber toward MB (c_0 = 2000 mg L^{-1}) and MO (c_0 = 2000 mg L^{-1}) at different temperatures. Plots of $\ln Q_e/c_e$ against 1/T for the adsorption of MB and MO on PA-COF nanofiber.

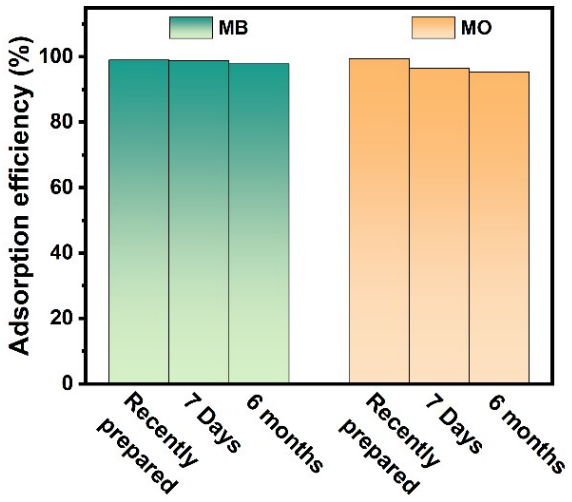


Fig. S13. Adsorption efficiency of dye MB/MO (50 mg L^{-1}) on PA-COF nanofiber.

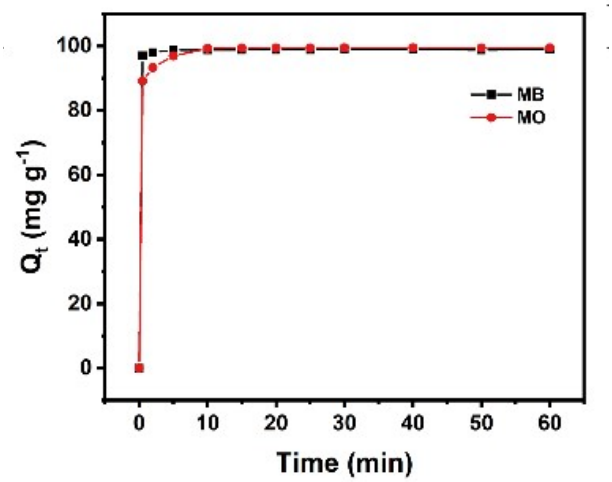


Fig. S14. Adsorption kinetics of PA-COF nanofiber toward aqueous MB (c_0 = 50 mg L^{-1}) and MO (c_0 = 50 mg L^{-1}) at 25 °C.

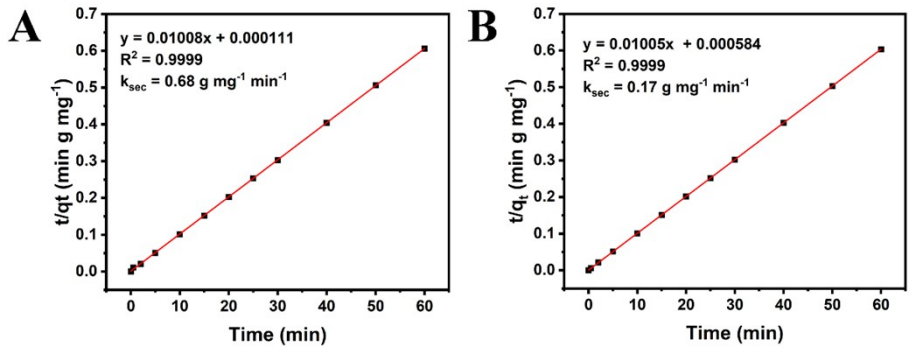


Fig. S15. Pseudo-second-order kinetic plots of PA-COF nanofiber toward (B) MB and (C) MO.

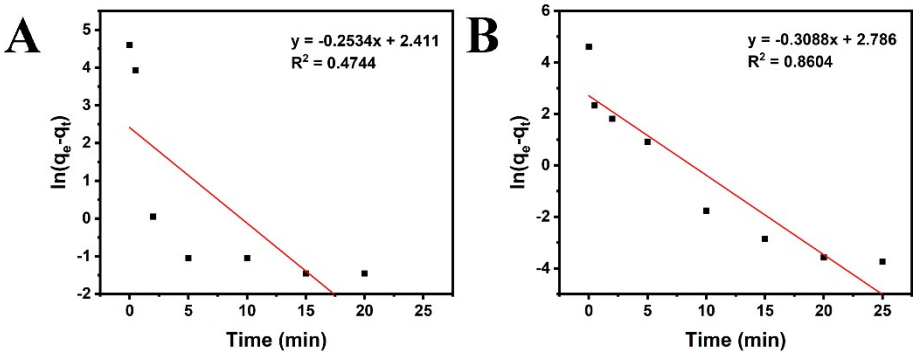


Fig. S16. Pseudo-first-order kinetic plots of PA-COF nanofiber toward (A) MB and (B) MO.

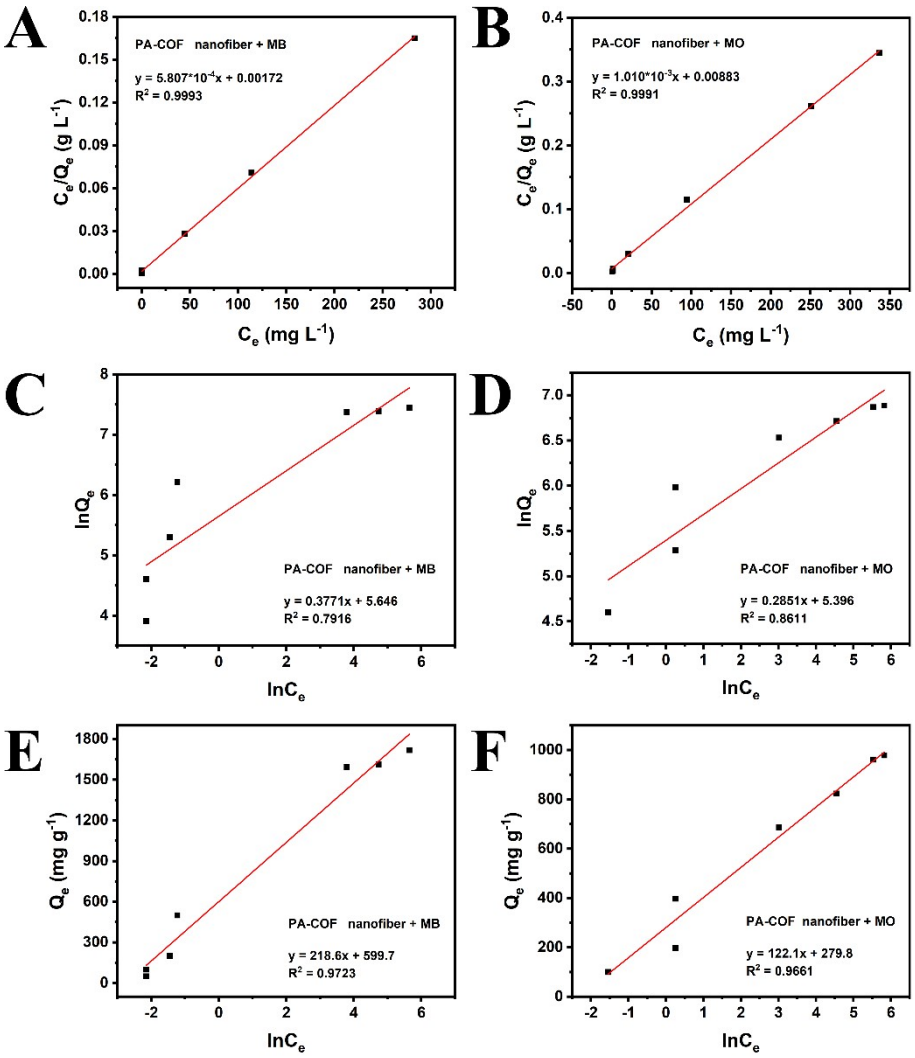


Fig. S17. Plots of the fitting of PA-COF nanofiber towards (A) MB and (B) MO adsorption experimental data with Langmuir isotherm mode. Plots of the fitting of PA-COF nanofiber towards (C) MB and (D) MO adsorption experimental data with Freundlich isotherm mode. Plots of the fitting of PA-COF nanofiber towards (E) MB and (F) MO adsorption experimental data with Temkin isotherm mode.

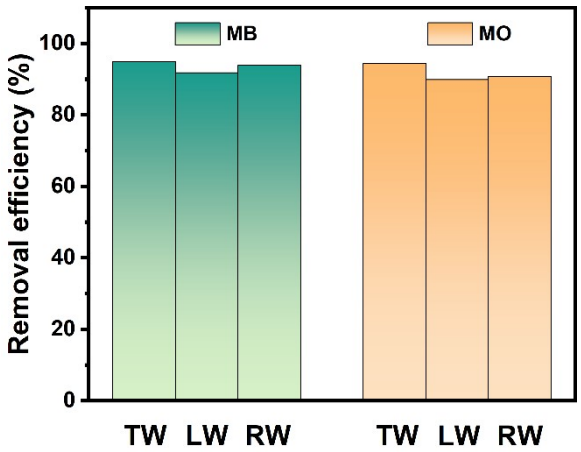


Fig. S18. Removal efficiencies of PA-COF nanofiber to dyes in real water samples. Tap water (TW); River water (RW); Lake water (LW).

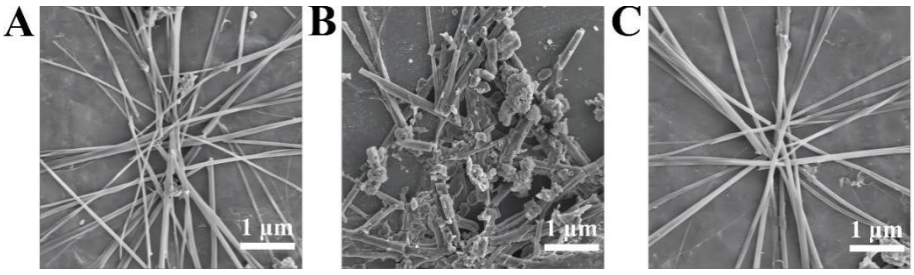


Fig. S19. SEM images of PA-COF nanofiber (A) before, (B) at equilibrium and (C) after dyes adsorption.

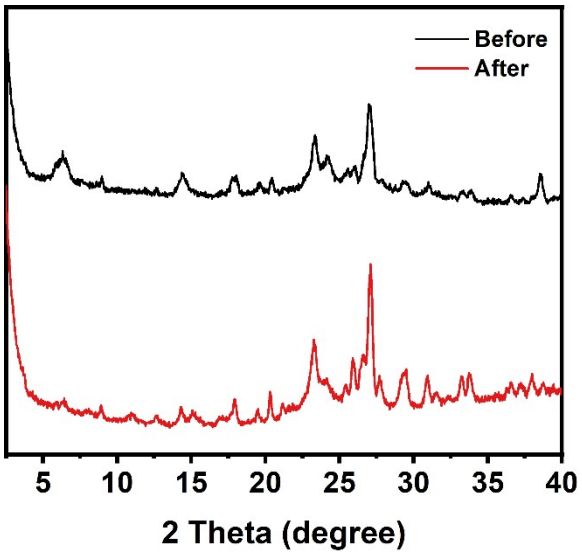


Fig. S20. XRD pattern of the PA-COF nanofiber before and after dye adsorption.

Table S1. The structures and sizes of dyes used in this work.

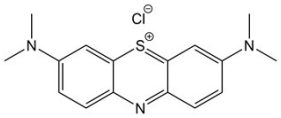
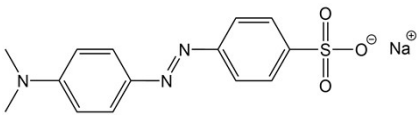
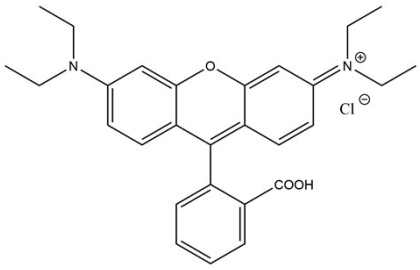
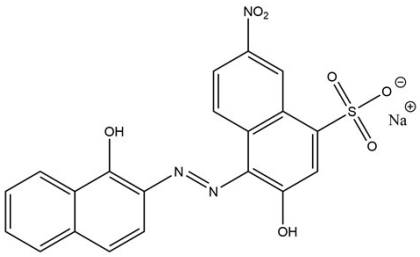
Dyes	Structure	Charge	Length, X (nm)	Width, Y (nm)	Height, Z (nm)
MB		+1	1.48	0.60	0.23
MO		-1	1.59	0.53	0.33
RhB		+1	1.69	0.90	0.45
EBT		-1	1.52	0.82	0.34

Table S2. The thermodynamic parameters for the adsorption of MB and MO on PA-COF nanofiber.

Dyes	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} k^{-1})	ΔG (kJ mol^{-1})			
			298 K	308 K	318 K	328 K
MB	39.55	146.16	-43.52	-44.98	-46.44	-47.90
MO	15.26	84.29	-25.10	-25.95	-26.79	-27.63

Table S3. The equilibrium capacities, rate constant and correlation coefficient R^2 of dyes adsorption on PA-COF nanofiber.

Kinetic models	Parameter	Dyes	
		MB	MO
Pseudo-first order	Q_{exp} (mg g^{-1})	99.07	99.41
	Q_{cal} (mg g^{-1})	4.289	16.22
	k_1 (min^{-1})	0.1371	0.3132
	R^2	0.7671	0.8391
Pseudo-second order	Q_{cal} (mg g^{-1})	98.91	99.50
	k_2 (g mg^{-1} min^{-1})	0.6800	0.1700
	R^2	0.9999	0.9999