

Supporting Information

Emissive organogel mediated construction of a flexible
covalent organic polymer for the separation of aniline
for water purification

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Section 1: Experimental Section

Materials and Methods

6-Hydrazinonicotinic hydrazide hydrate, benzene-1,3,5-tricarboxaldehyde, dimethyl sulfoxide (DMSO), *N,N*-dimethyl acetamide and all solvents were purchased from Merck. The chemical shifts (δ) were reported in ppm.

Section 2: Synthesis of COP via Organogel Formation

6-Hydrazinonicotinic hydrazide hydrate (20 mg, 0.12 mmol) and benzene-1,3,5-tricarboxaldehyde (13 mg, 0.08 mmol) were taken in 1 mL *N,N*-dimethyl acetamide solution in 5 mL glass vial and sonicated for 5 min. After that 2 μ L 1N HCl was added to the solution mixture and sonicated for another 1 min to form a gel. To obtain pure **COP** powder, the **COP-gel** was dried and washed several times with water, ethyl acetate, *N,N*-dimethyl formamide and methanol.

Section 3: Thin Film Preparation

6-Hydrazinonicotinic hydrazide hydrate (15 mg, 0.09 mmol) and benzene-1,3,5-tricarboxaldehyde (9.7 mg, 0.05 mmol) were taken in 2 mL *N,N*-dimethyl acetamide solution in 50 mL beaker and sonicated for 5 min. After that 5 μ L 1N HCl was slowly added to the solution mixture followed by sonication. The solution mixture was then heated to 60 °C and then cooled to 25 °C until a film formed. Then it was washed with boiled water and heated at 60 °C again for 15 min. Next, the thin film was taken out from beaker using a blunt blade spatula.

Section 4: Preparation of Solution for UV-Vis and Fluorescence Experiment

3 mg of **COP** powder was added into 2 mL of DMA solution and sonicated for 15 min. After that disperse solution of **COP** in DMA solvent was used for experiment.

Section 5: Steady-state Absorption and Fluorescence Measurement

Steady state UV-vis absorption measurements were carried out using Varian Cary 100 Bio UV-Visible Spectrophotometer with 1 cm path length quartz cuvette. All steady-state emission measurements were investigated using HORIBA Jobin Yvon Fluorolog fluorimeter using Origin 8.1 software provided with the instrument. Fluorescence spectra were carried out using 1 cm path length quartz cuvette using HORIBA Jobin Yvon, model (FM-100) and keeping both excitation and emission slit at 5 nm.

Section 6: Confocal Imaging of COP

For confocal imaging of **COP**, confocal microscope from OLYMPUS (model IX-83) was used. A Multiline Ar laser (gas laser) with an excitation wavelength of 405 nm was used. The mode of observation was LSM (laser scanning microscopy). The scan mode was XY and the scan direction was one way. The samples were immobilized on a clean cover slide by simple drop casting method. All images were taken at ambient temperature.

Section 7: Material Characterization

Solid state ^{13}C NMR spectra was carried out on solid state NMR spectrometer (JEOL, model: ECX400; proton frequency: 400 MHz). Powder XRD was done on Rigaku SmartLab, Automated Multipurpose X-ray Diffractometer. Thermogravimetric analysis (TGA) was analyzed using Mettler Toledo Thermal Analyzer with heating rate of 10 °C/min. BET surface area was performed on quantachrome, Autosorb iQ2. FT-IR spectra of **COP** were carried out using Bruker (Tensor-27) FT-IR spectrophotometer. High resolution transmission electron microscopy (HRTEM) analysis was performed using Field Emission Gun-Transmission Electron Microscope 300 kV (model no Tecnai G2, F30). The field-emission scanning electron microscopy (FESEM) was evaluated using a field-emission scanning electron microscope, Supra 55 Zeiss. Atomic force microscopy (AFM) measurements were performed on a cleaned glass coverslip using smart scan software (model park NX10) in tapping mode.

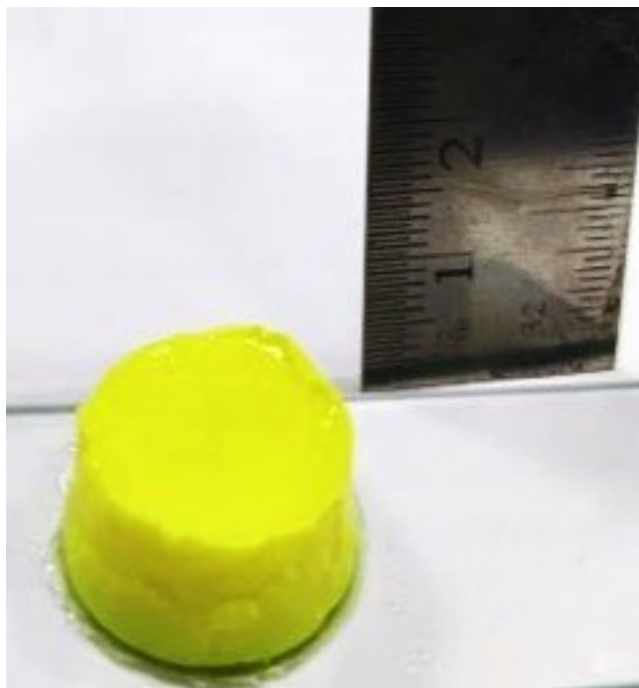


Fig. S1 3D block representation of **COP-gel**. 6-Hydrazinonicotinic hydrazide hydrate (60 mg, 0.35 mmol) and benzene-1,3,5-tricarboxaldehyde (38 mg, 0.23 mmol) were taken in 5 mL *N,N*-dimethyl acetamide (DMA) solution in 15 mL glass vial. Then the solution mixture was sonicated for 5 min. After that 15 μ L 1N HCl was added to the solution mixture. It was then sonicated for another 2 min to form the gel.

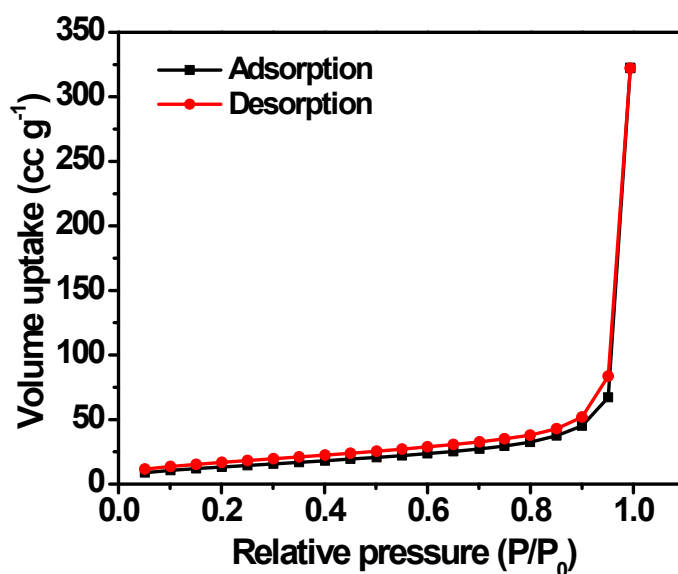


Fig. S2 BET surface area analysis of **COP** by nitrogen sorption.

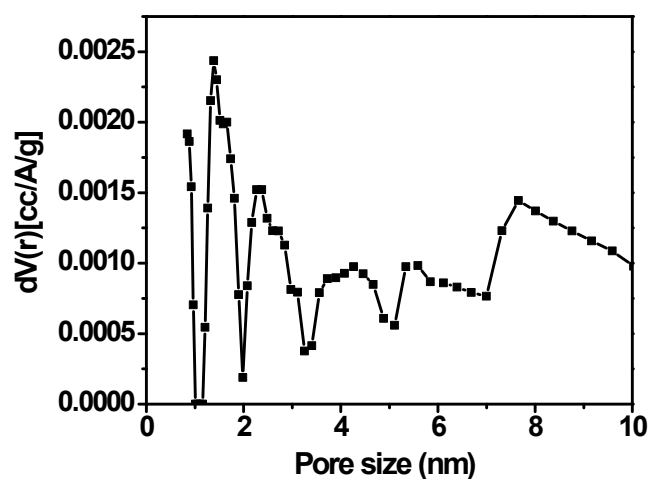


Fig. S3 Pore size distribution curve of **COP** by NLDFT method.

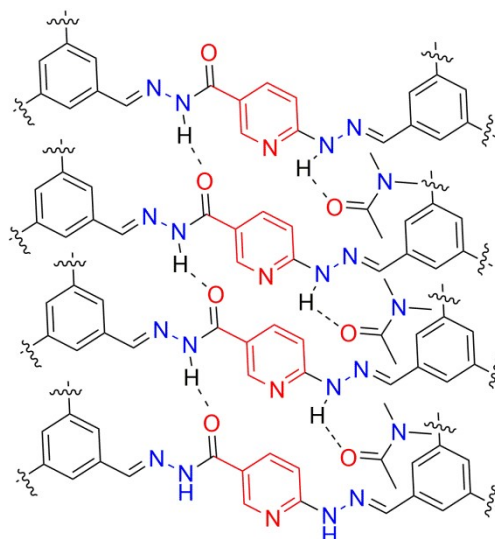


Fig. S4 Schematic representation of intermolecular H-bonding inside the **COP**.

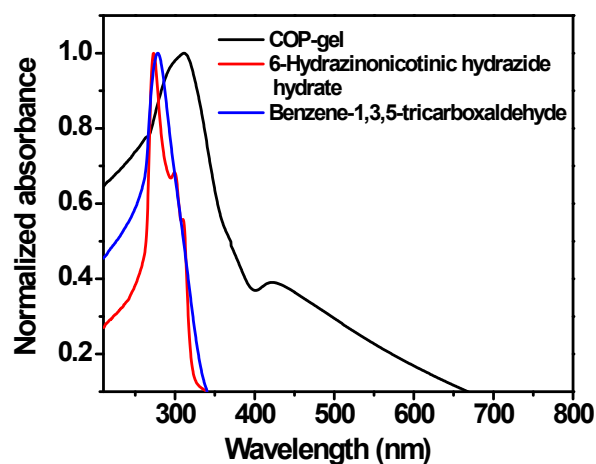


Fig. S5 UV-vis absorption spectra of **COP-gel**, 6-hydrazinonicotinic hydrazide hydrate and benzene-1,3,5-tricarboxaldehyde.

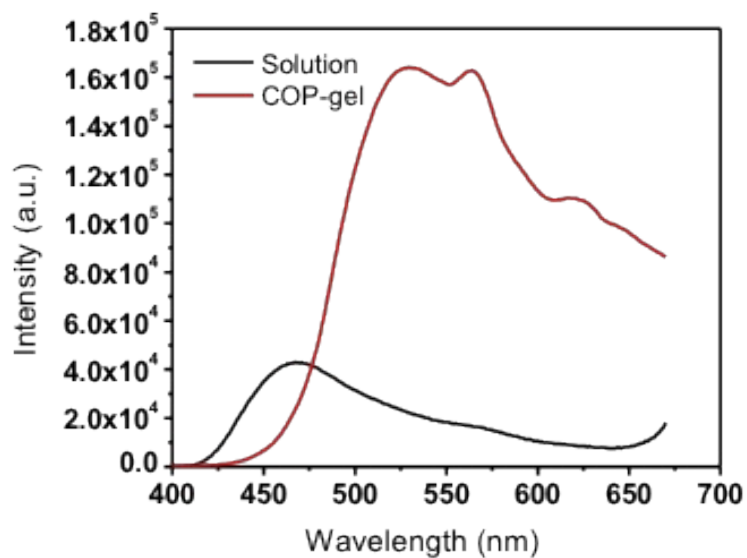


Fig. S6 Emission spectra of COP-gel and solution mixture of 6-hydrazinonicotinic hydrazide hydrate and benzene-1,3,5-tricarboxaldehyde in DMA solvent ($\lambda_{\text{ex}} = 340$ nm).

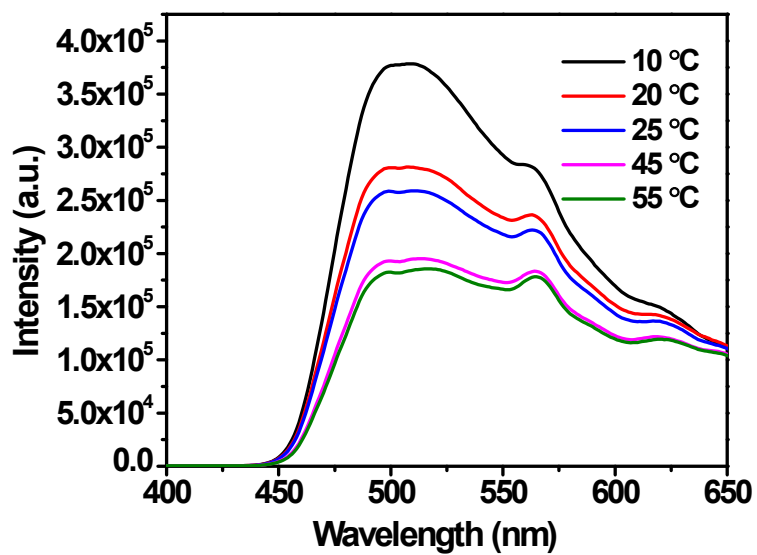


Fig. S7 Emission spectra of COP-gel at different temperature ($\lambda_{\text{ex}} = 340$ nm).

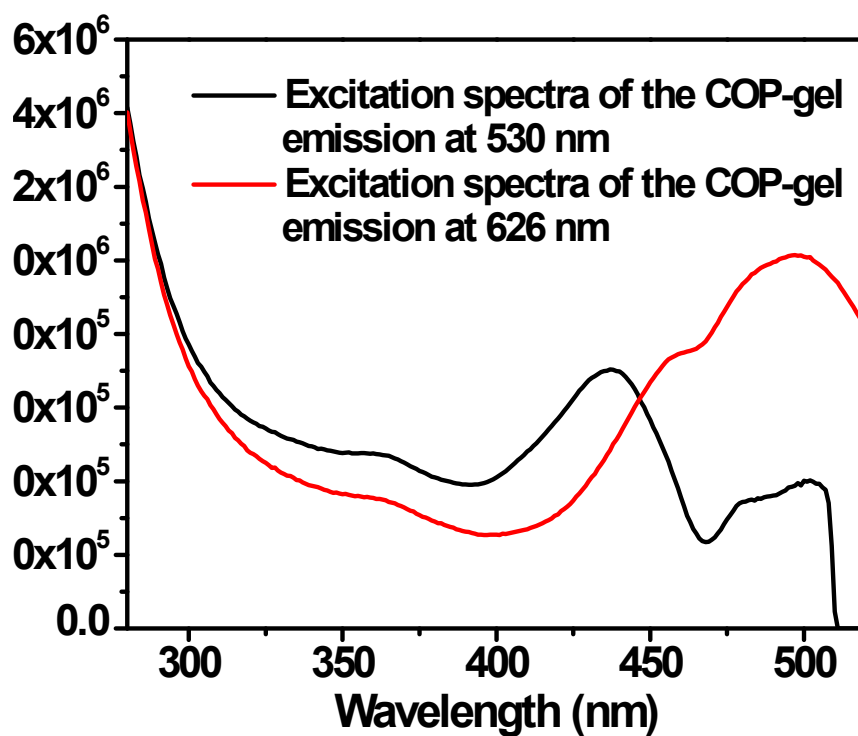


Fig. S8 Excitation spectra of COP-gel (λ_{em} at 530 and 626 nm).

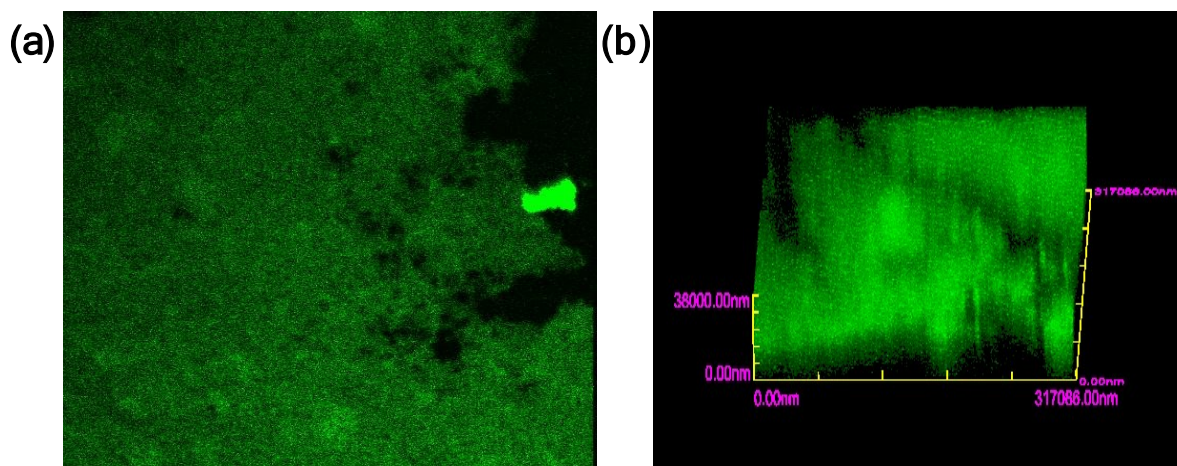


Fig. S9 (a) Confocal image of COP. (b) Confocal 3D image (with z-axis interpretation) of COP.

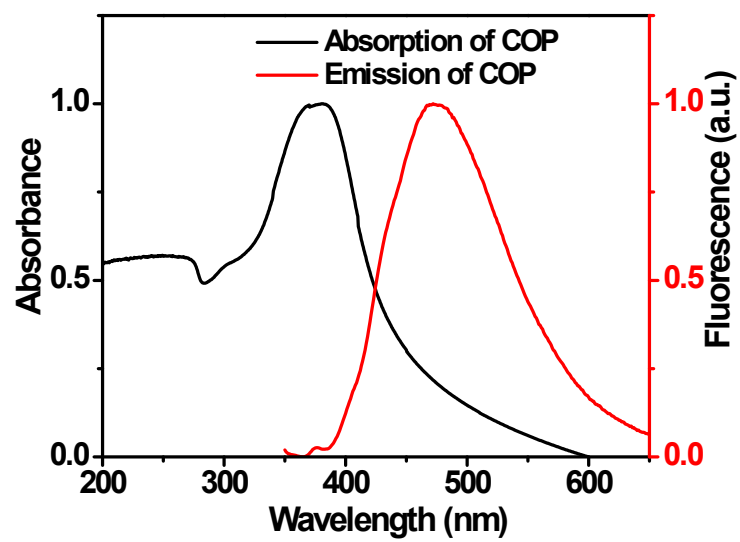


Fig. S10 Absorption and emission spectra of COP in DMA.

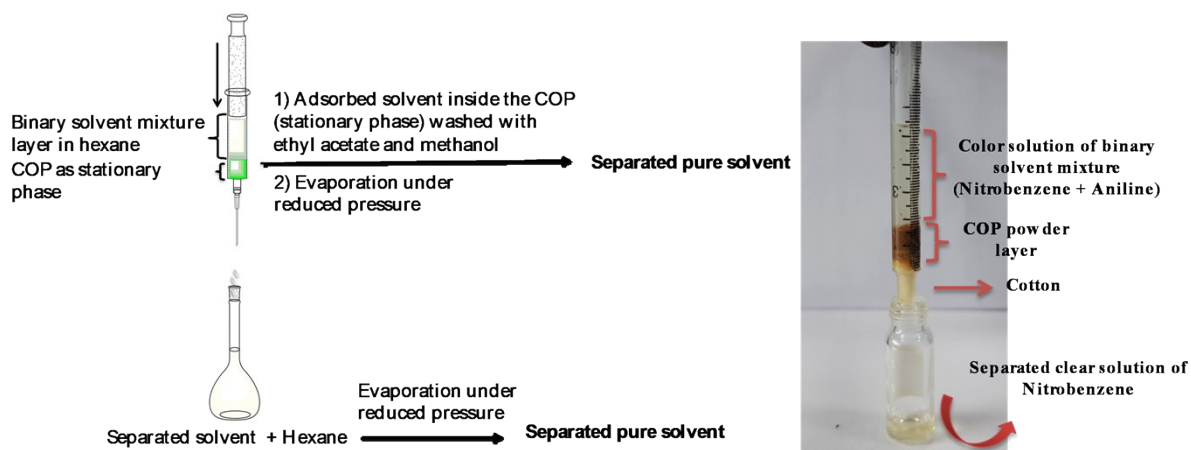


Fig. 11 Schematic presentation and optical image for the separation of binary solvent mixture using COP.

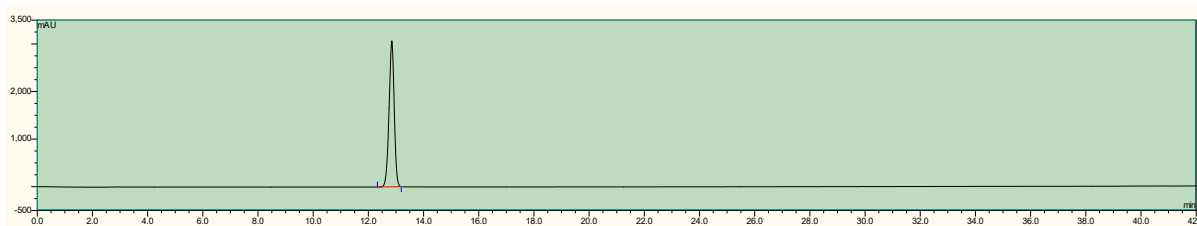


Fig. S12 HPLC chromatogram of nitrobenzene (control experiment).

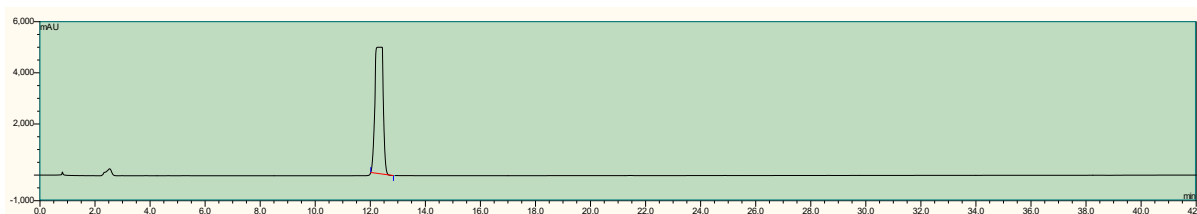


Fig. S13 HPLC chromatogram of nitrobenzene separated out from the nitrobenzene/aniline mixture.

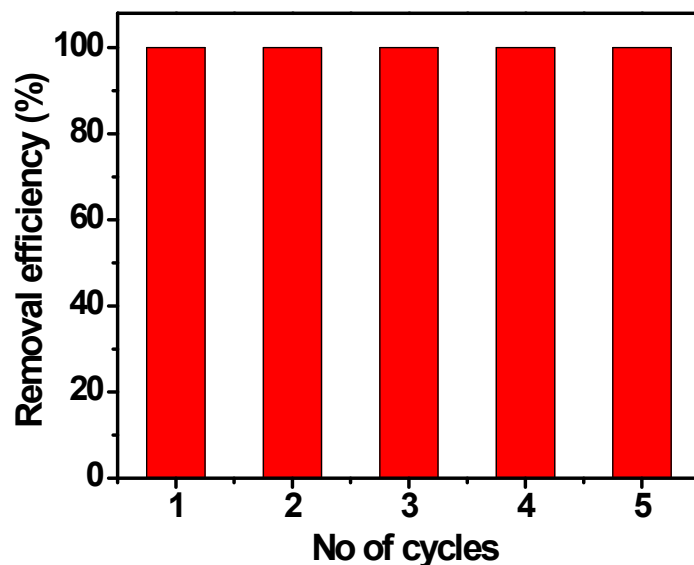


Fig. S14 Recyclability histograms of aniline separation using the COP powder.

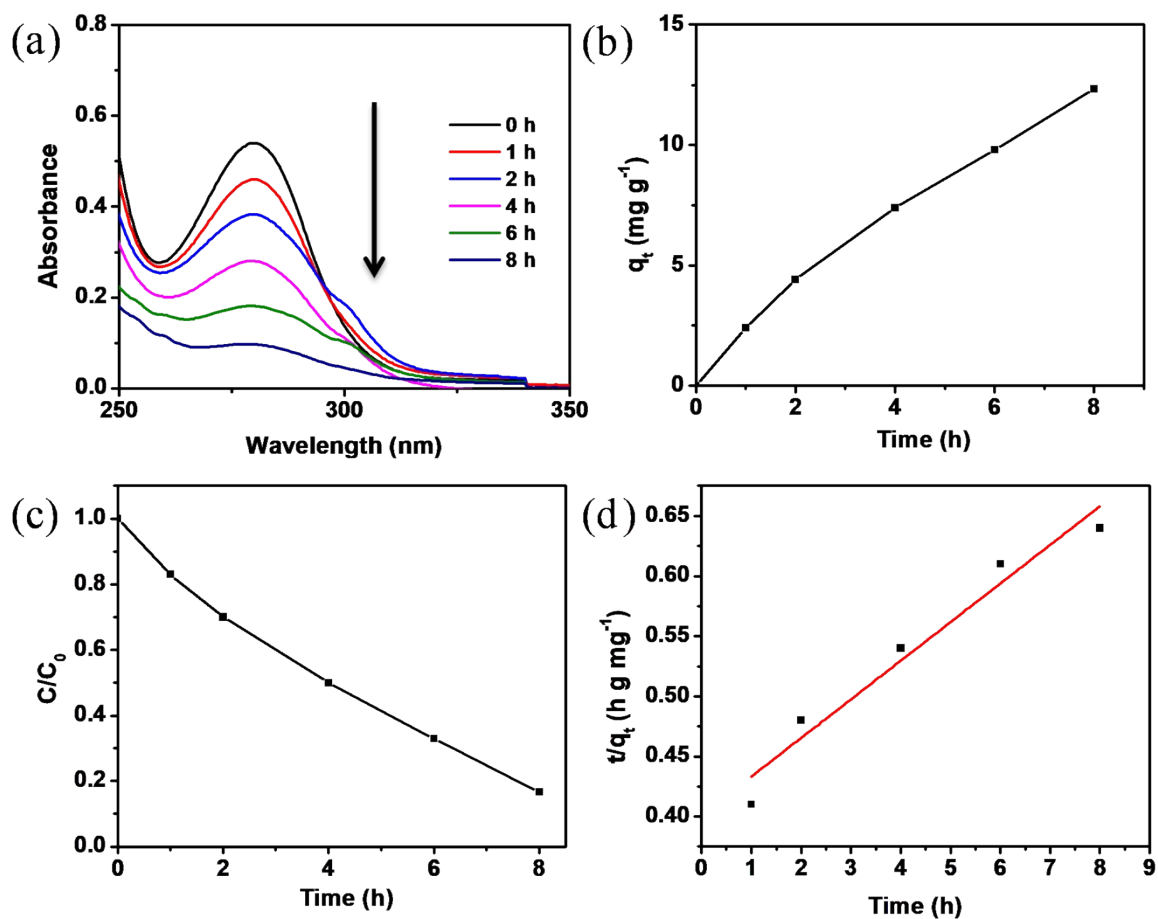


Fig. S15 (a) Time-dependent UV-Vis spectra of 45 mg of COP in 222 mg L^{-1} of aniline solutions in water. (b) and (c) Effect of contact time on the adsorption of aniline by COP at the initial concentration of 222 mg L^{-1} . (d) Pseudo-second-order kinetic plot for the adsorption of aniline by COP.

Section 8: Extraction of aniline from water using COP

The efficiency of removing aniline from water is calculated by using following equation

$$\text{Removal percentage (\%)} = \frac{(C_0 - C_e) \times 100}{C_0} \quad \text{Eq. S1}$$

where, C_0 is the initial concentration of aniline in water and C_e is the equilibrium concentration (final concentration) of the aniline.

The maximum adsorption capacity of COP is calculated as follows,

$$q_e = \frac{(C_0 - C_e)V}{m} \quad \text{Eq. S2}$$

where, C_0 is the initial concentration, C_e is the equilibrium (final concentration) concentration, and V is the volume of solution taken in mL and m is the mass of COP taken for the experiment.

The pseudo-second-order rate constant for the aniline adsorption kinetics of COP and the adsorption rate are calculated by using following equation,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Eq. S3}$$

where, k_2 ($\text{g mg}^{-1} \text{h}^{-1}$) is the rate constant of adsorption, q_e is the equilibrium adsorption capacity and q_t is the adsorption capacity at time t. The initial adsorption rate is assigned as $(k_2 q_e^2)$.

The adsorption of aniline was calculated (q_t) at different time intervals (Fig. S15b and c), where q_t represents the corresponding adsorption at specific time t (Eq. S2). The COP achieves a maximum aniline adsorption capacity (q_e) of 12.5 mg g^{-1} (using Eq. S2) from water solution. The pseudo-second-order rate constant was investigated to simulate the adsorption kinetics of COP for aniline, and the linear forms of the pseudo-second order kinetics model for aniline is expressed by Eq. S3 (Fig. S15d). The initial adsorption rate, $(k_2 q_e^2)$, is calculated as $2.5 \text{ mg g}^{-1} \text{h}^{-1}$. It is demonstrated that the kinetic data agree well with the pseudo second-order model. Even after third adsorption cycles, COP still can remove more than 60% of aniline from the aqueous solution.