Supporting Information

1. Experimental Section

1.1 Chemicals

Biphenyl (99%, Aladdin), anhydrous AlCl₃ (99%, Aladdin), Brij® C10 (99%, Sigma), tetraethyl orthosilicate (TEOS) (99%, Acros) and 3-aminopropyltrimethoxysilane (APTS) (99%, Aladdin) were purchased from the corresponding chemical companies. P123, ethyl acetate (CH₃COOC₂H₅), tetrahydrofuran (THF), chloroform (CHCl₃), methanol (CH₃OH), acetone (CH₃COCH₃), ethanol (C₂H₅OH) and hydrochloric acid (HCl) were commercially supplied.

1.2.1 Synthesis of hard templates

SBA-15: 2.0 g of P123 was dissolved in 65 g of deionized water with 10 ml concentrated hydrochloric acid, and the mixture was stirred at 38 °C until a homogeneous solution was obtained. Then, 4.16 g of TEOS was added into the above solution and kept under stirring at 38 °C for 24 h. The mixture solution was transferred into an autoclave and hydrothermally treated for 24 h at 100 °C. The white solid powder was obtained by filtration, washed with distilled water, dried at 80 °C overnight, and calcined in air at 550 °C for 6 h to remove the surfactant.

B56-E-20: 4.8 g of Brij-56 was dissolved in 180 g of deionized water along with 0.3 g of APTS and 0.462 g of ethyl acetate under stirring for half an hour at room temperature, and then 4.8 g of TEOS was added to the above mixture. Then, the solution was kept under stirring for another 24 h at room temperature. The mixture solution was transferred into an autoclave and hydrothermally treated for 24 h at 100 °C. The white solid powder was obtained by centrifugation, washed with distilled water, dried at 80 °C overnight, and calcined in air at 550 °C for 6 h to remove the surfactant.

1.2.2 Synthesis of the PAF-45 material

PAF-45: 1000 mg anhydrous AlCl₃ was added into a 250 ml round-shaped flask, and this flask was first evacuated and then inflated with N₂ for 3 times. 60 ml dried CHCl₃ was injected into the flask via a syringe and the mixture was heated to 60 °C for 3 h. Another solution containing 400 mg biphenyl in 40 ml dried CHCl₃ was added into
the above solution and the mixture was kept under stirring at 60 °C for 24 h. After reaction, the raw powder was collected by filtration and washed with 1.0 M HCl, CH₃OH, and acetone. The brown powdered sample was further purified by Soxhlet extraction with C₂H₅OH, THF, and CHCl₃ for 48 h. The final product was obtained after drying at 120 °C for 12 h in vacuum.

### 1.2.3 Synthesis of PAF-45@SBA-15 and PAF-45@B56-E-20 hybrid materials

All hybrid materials were prepared by modifying the synthesis procedure for PAF-45. In detail, 200 mg well-dried hard template (SBA-15 or B56-E-20) was added to a 100 ml round-shaped flask and kept under vacuum. 200 mg biphenyl dissolved in 15 ml dried CHCl₃ was added into the flask and stirred for 2 h at room temperature. The flask was inflated with N₂ and then 700 mg anhydrous AlCl₃ was added in. The mixture in the flask was stirred for 24 h under reflux. After filtration, the brown solid was first washed with 1.0 M HCl, anhydrous alcohol and acetone, and then solvent exchanged with anhydrous acetone 3-4 times, and finally dried under vacuum for 12 h at 120 °C to give the target product.

### 1.2.4 Synthesis of PAF-45HX (PAF-45HS and PAF-45HB)

200 mg of PAF-45@SBA-15 or PAF-45@B56-E-20 was added into 5% HF (10 ml) aqueous solution and stirred for 24 h under room temperature. And then, the product was obtained by filtrated, washed with water, and repeated this process for three times. The final product was dried at 120 °C for 12 h.

### 1.3 Characterizations

FT-IR spectra were taken on a Bruker IFS 66v/S Fourier transform infrared (FT-IR) spectrometer. Thermogravimetric analysis (TGA) was recorded on a Netzch Sta 449c thermal analyzer system at a heating rate of 10 °C min⁻¹ in an air atmosphere. Transmission electron microscopy (TEM) was performed using a JEOL JEM 3010 instrument with an acceleration voltage of 300 kV. Scanning electron microscopy (SEM) analysis was performed on a JEOL JSM 6700 system equipped with energy-dispersive X-ray spectroscopy (EDX). X-ray diffraction (XRD) tests were carried out on a Rigaku SmartLab X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å) at 40 kV and 30 mA. The N₂ adsorption-desorption isotherms were measured on a
Quantachrome Autosorb-iQ2 analyzer at 77 K. The uptake for Rhodamine B was evaluated by adding 10 mg PAF-45 (PAF-45HS) into 10 ml Rhodamine B aqueous solution under stirring for 24h at room temperature. The maximum uptake for Rhodamine B on PAF-45 or PAF-45HS was calculated based on amounts adsorbed in Rhodamine B solutions with different concentrations (6, 8, 20 and 40 mg l$^{-1}$ for PAF-45; and 50, 100, 150, 250 and 350 mg l$^{-1}$ for PAF-45HS) using the following equation:
\[
\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{Kq_m}
\]
where \(c_e\) (mg l$^{-1}$) is the equilibrium solute concentration, \(q_e\) (mg g$^{-1}$) is the equilibrium adsorption capacity, \(q_m\) (mg g$^{-1}$) is the maximum adsorption capacity, and the constant \(K\) is related to the adsorption energy.

The kinetic data for measuring the rate constant was acquired by monitoring the changes of Rhodamine B concentrations in the solutions (10 ml, 20 mg l$^{-1}$) on 10 mg PAF-45 or PAF-45HS with a function of time (5, 25, 60, 90, 120 mins) at room temperature. The concentrations of Rhodamine B were measured by UV-Vis spectrophotometer (UV-2450). The rate constant for adsorbing Rhodamine B was calculated according to the equation below:
\[
\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{kq_e^2}
\]
where \(q_t\) (mg g$^{-1}$) is the adsorption capacity at any time, \(q_e\) (mg g$^{-1}$) is the equilibrium adsorption capacity, \(t\) (min) is the time, and \(k\) (g mg$^{-1}$ min$^{-1}$) is the rate constant.
2. Supplementary Figures

**Fig. S1** TGA curves for biphenyl@SBA-15 (a) and biphenyl@B56-E-20 samples (b) after loading biphenyl initial reactants into the silica with subsequent thorough wash using CHCl₃.

**Fig. S2** FT-IR spectra for (a) SBA-15, PAF-45@ SBA-15, PAF-45 and PAF-45HS samples; and (b) B56-E-20, PAF-45@B56-E-20, PAF-45 and PAF-45HB samples.
Fig. S3 EDX spectra for (a) PAF-45@SBA-15, (b) PAF-45HS, (c) PAF-45@B56-E-20, and (d) PAF-45HB samples.
Fig. S4 TGA curves for (a) PAF-45@SBA-15, PAF-45 and PAF-45HS samples; and (b) PAF-45@B56-E-20, PAF-45 and PAF-45HB samples.

Fig. S5 SEM images of SBA-15 (a), PAF-45@SBA-15 (b), PAF-45HS (c), B56-E-20 (d), PAF-45@B56-E-20 (e), and PAF-45HB (f).
Fig. S6 (a) Equilibrium adsorption isotherms of Rhodamine B (RB), (b) the variations of RB concentrations with the contact time (inset is the photo of RB at 0 and 120 min), (c) the linear fits of the equilibrium adsorption data using the Langmuir model, and (d) the linear plots of adsorption kinetics using the pseudo-second order model on PAF-45 and PAF-45HS.