Contents lists available at ScienceDirect

Polymer



journal homepage: www.elsevier.com/locate/polymer

Tetraphenylpyrene-bridged silsesquioxane-based fluorescent hybrid porous polymer with selective metal ions sensing and efficient phenolic pollutants adsorption activities

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ARTICLE INFO

Keywords: Silsesquioxane Porous polymer Phenolic pollutants Ion sensing

ABSTRACT

A silsesquioxane based fluorescent porous polymer (PCS-TPPy) was easily prepared by Friedel-Crafts reaction of tetraphenylpyrene (TPPy) with octavinylsilsesquioxane (OVS) using AlCl₃ as catalyst. PCS-TPPy exhibited a high porosity with a Brunauer-Emmet-Teller surface area of 1236 m² g⁻¹ and total pore volume of 0.98 cm³ g⁻¹. The excellent fluorescence of PCS-TPPy has enabled it to have sensitive and selective sensing capability for Ru³⁺ and Fe³⁺ with good linear response from 10 to 1000 μ M and the corresponding detection limits are 3.12 μ M and 6.78 μ M, respectively. Moreover, high surface area, hierarchical microporous/mesoporous structure and conjugated structure of tetraphenylpyrene unit in this material favor phenolic pollutants adsorption with an excellent adsorption capacity of 1.53 mmol g⁻¹ for 4-bromo-phenol (BP), 0.68 mmol g⁻¹ for hydroquinone (HQ) and 0.50 mmol g⁻¹ for phenol (PH), respectively. Importantly, PCS-TPPy exhibits an excellent regeneration performance.

1. Introduction

Air, water and soil are now polluted by human activities to varying degrees [1–3], therefore, the world is facing serious challenges from environmental pollution [4]. As two kinds of important pollutants, metal ions (Hg^{2+} , Pb^{2+} , Ru^{3+} , Gd^{3+}) and phenolic substances (organic pollutants) have serious impacts on environmental safety, human life and health [2,5–10]. Although some metal ions (Zn^{2+} , Ca^{2+} , Mg^{2+} , Fe^{3+}) are beneficial and essential to human body, they will also have an adverse effect on human body due to the oversaturation caused by bioaccumulation [11–13]. Therefore, it is of great significance to accurately detect and remove these pollutants for environmental protection and human health [14].

Compared with traditional porous materials such as activated carbon and zeolite [15,16], covalently-linked porous polymers as new fast-growing solid materials have attracted a lot of attention for their potential applications in catalysis, detection, gas storage and adsorption due to the flexibility of synthesis methods, a wide range of selected monomers and excellent performances [17–20]. Among them, fluorescent porous polymers are extremely interesting because the fluorescence could endow the porous polymer with new functions that are of great importance in different applications, for example, sensor, bio-imaging, photodynamic therapy and light-emitting diode [21–24].

Different kinds of fluorescent units, such as tetraphenylethene (TPE), hexaphenylsilolev (HPS), triphenylamine (TPA), spirobifluorene and carbazole have been successfully introduced to prepare covalentlylinked fluorescent porous materials [25–29]. Besides, the large surface area and pore volume can significantly facilitate adsorption through the rapid diffusion of guest molecules into the porous internal surface. Therefore, it is desirable to further design and prepare novel fluorescent porous polymers for efficient adsorption and detection of pollutants for environment protection.

Cage silsesquioxanes (SQs) have proven to be ideal building blocks to construct hybrid porous polymers due to their rigid structure and multifunctionality [30–33]. A series of novel organic-inorganic hybrid silsesquioxanes-based porous polymers containing multiple organic functional groups could be prepared by Friedel-crafts reaction, Heck reaction, thiol-ene reaction and cationic polymerization using

https://doi.org/10.1016/j.polymer.2021.124083

Received 31 May 2021; Received in revised form 25 July 2021; Accepted 6 August 2021 Available online 7 August 2021 0032-3861/© 2021 Elsevier Ltd. All rights reserved.





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octavinylsilsesquioxane (OVS) as a starting material [25,27,34,35]. Friedel-Crafts reaction of OVS with different fluorescent monomers is a feasible method to prepare hybrid fluorescent porous polymers [36]. For example, Meng et al. successfully prepared a series of silsesquioxane-carbazole-corbelled hybrid porous polymers with controllable porosity and excellent luminescence property, which could serve as a metal-free heterogeneous catalyst for the cycloaddition reaction of CO₂ with epoxide to form cyclic carbonate [37]. Due to their rigidity and excellent luminescence, a series of pyrene derivatives have been used to prepare COFs or MOFs as the fluorescent probes in the past decade [38-41]. However, the combination of pyrene unit and silsesquioxane unit, which can offer hybrid porous polymers with improved fluorescence and stability, has not received adequate attention by far. Our group once prepared two kinds of fluorescent hybrid porous polymers by Friedel-Crafts and Heck reaction of OVS with pyrene and brominated pyrene [28,42], respectively, which could be applied in the field of detection and adsorption. Compared with pristine pyrene, 1,3,6,8-tetraphenylpyrene (TPPy) is a kind of fluorescent chromophore with stronger fluorescence performance, which has high hole transport performance with high quantum yield in both solution and solid state [43]. In order to further improve the fluorescence of silsesquioxanes-based porous polymer, we select octavinylsilsesquioxane (OVS) and 1,3,6,8-tetraphenylpyrene (TPPy) as building blocks to construct a new hybrid fluorescent porous polymer (PCS-TPPy) by Friedel-Crafts reaction in this paper, which shows more sensitive and selective sensing properties compared with other similar polymers (Table S1). After introducing the TPPy unit into the hybrid cross-linked network, as shown in Table S3, it can be found that the specific surface area, micropore area and micropore volume of PCS-TPPy increase except improved fluorescence compared with the pyrene-based porous materials [28b,42]. The detection of metal ions and adsorption of phenolic pollutants are further investigated using PCS-TPPy. More importantly, it offers an excellent regeneration performance.

2. Experimental

2.1. Materials

Unless otherwise mentioned, all reagents were purchased from commercial suppliers and used without further purification. 1,2-dichloroethane was dried by distillation over CaH_2 about two days.

2.2. Synthesis of 1,3,6,8-tetraphenylpyrene (TPPy)

TPPy was synthesized as described in a previous publication [44]. 1, 3,6,8-Tetrabromopyrene (200 mg, 0.386 mmol), phenylboronic acid (254 mg, 2.08 mmol), Pd(PPh₃)4 (50 mg, 0.04 mmol) and 2.0 M NaOH aqueous solution (2 mL) were mixed in a flask containing nitrogen saturated toluene (10 mL). The reaction mixture was stirred at 90 °C for 24 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane (2 \times 40 mL). The combined organic extracts were dried with anhydrous magnesium sulfate and evaporated. The crude product was purified by column chromatography using a 1:5 petroleum ether/ethyl acetate mixture as the eluent to provide a light-colored powder and recrystallized from hexane to obtain 1,3,6, 8-tetraphenylpyrene (TPPy) as a light yellow powder (125 mg, 63%): IR *v*_{max} (KBr) 2960, 1600, 1513, 1494, 1459, 1286, 1245, 1176, 1106, 1035, 835, 549, 476 cm-1;¹H NMR (400 MHz, CD₂Cl₂) δ 7.36–7.40 (m, 4H), 7.47 (t, J = 7.6 Hz, 8H), 7.61 (d, J = 8.0 Hz, 8H), 7.98 (s, 2H), 8.12 (s, 4H); 13 C NMR (125 MHz, CDCl₃) δ 141.10, 137.28, 130.68, 129.57, 128.37, 128.15, 127.32, 125.97, 125.35; *m/z* 506.1948(M+).

2.3. Synthesis of TPPy-bridged silsesquioxane-based hybrid porous polymer (PCS-TPPy)

OVS (0.32 g, 0.5 mmol), TPPy (0.13 g, 0.25 mmol), and anhydrous

aluminum chloride (AlCl₃) (0.14 g, 1 mmol) were added to a threenecked flask with 25.0 mL 1, 2-dichloroethane under nitrogen protection. The mixture was stirred at room temperature for 1 h, then heated to 85 °C for one day. After the reaction, the mixture was cooled to room temperature and filtrated. The solid was washed with methanol, THF and acetone successively to remove unreacted monomer and catalyst. The resulting product was further purified in a Soxhlet extractor with methanol for 24 h and dichloromethane for another 24 h, finally dried under vacuum at 75 °C to obtain a grey solid (0.56 g, 98%).

2.4. Detection of metal ions

The detection of metal ions is of great significance in ecological and environmental safety. PCS-TPPy is a cross-linked polymer with an excellent fluorescence property; therefore, it could act as a sensor to detect metal ions heterogeneously. Metal ions (Ru^{3+} , Fe^{3+} , Fe^{2+} , Ca^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} , Cu^{2+} , Sr^{2+} , Cd^{2+}) were dissolved in deionized water to form a solution, then PCS-TPPy (3.0 mg) was added to 10.0 mL of metal ion solution, which consisted of equal volumes of water and absolute ethanol. Ru^{3+} and Fe^{3+} were selected for sensitivity analysis. Taking Ru^{3+} fluorescence detection sensitivity experiment as an example, PCS-TPPy (3.0 mg) was added to 10 mL equal volume of water and absolute ethanol in Ru^{3+} solutions to prepare suspensions with different concentrations. Finally, the limit of detection (LOD) for Ru^{3+} was calculated using eq (1) as follows:

$$LOD = 3 \times \sigma/S \tag{1}$$

where σ represents the standard deviation of blank measurement, which was obtained by recording the fluorescence intensity of the PCS-TPPy suspension in aqueous solution ten times. and S is the slope of the calibration of PCS-TPPy to $\rm Ru^{3+}$ or $\rm Fe^{3+}$ ions. Moreover, the BR buffer solution was chosen to explore the influence of pH changes on luminescence properties test. And then the effect of pH on the detection efficiency was investigated by adjusting the pH of the mixture containing $\rm Ru^{3+}$ or $\rm Fe^{3+}$ (10⁻³ mol/L) and PCS-TPPy suspension (3 mg/10 mL) in the pH range from 1 to 7. Hydrochloric acid and sodium hydroxide were used to adjust the pH.

2.5. Adsorption experiment

Phenols are typical refractory aromatic compounds in wastewater [9]. 4-bromo-phenol (BP), hydroquinone (HQ), and phenol (PH) were selected as representative pollutants to investigate the adsorption process of PCS-TPPy in this work. The pollutant samples to be tested were prepared by diluting the deionized jelly stock solution of BP, HQ and PH with the known amount. 3 mg PCS-TPPy was added to the pollutant solutions with different initial concentrations, stirred at room temperature for one day, and filtered to remove the adsorbent. Finally, the UV absorbance was measured and the equilibrium concentrations of phenolic pollutants in the filtrate were calculated.

2.6. Detection and adsorption in real water samples

OVS and TPPy are rigid and multifunctional molecules, which make them easy to construct stable hybrid porous polymer by Friedel-Crafts reaction. TPPy endows the porous polymer with excellent fluorescence and the introduction of silica-like cubic cages enhances the thermal stability of the hybrid polymers. In addition, cubic cage could prevent π - π stacking and enhance the fluorescence intensity. Therefore, the prepared silsesquioxane-based TPPy-functionalized porous polymers show high stability and fluorescence besides good porosity. Considering the porosity and fluorescence (Table S2, Fig. S7†), PCS-TPPy is chosen to be a representative material to explore its practical application. Detection and adsorption experiments were carried out by applying PCS-TPPy in three different types of real water (lake water of Daming Lake, spring water of Black Tiger Spring and pool water of Five Dragons Pool in Jinan, China) with different concentrations of metal ions (Ru^{3+} , Fe^{3+}) or phenolic pollutants (BP, HQ, PH). After applying PCS-TPPy in different real samples, the fluorescence emission intensity of the prepared samples is recorded. Then, a certain concentration of metal ions is added to the sample to test its fluorescence change (Fig. S10†). The results show that even in different actual water samples, PCS-TPPy can still effectively detect Ru^{3+} and Fe^{3+} . Moreover, three certain amounts of phenolic pollutants are added to the three actual water samples, then PCS-TPPy is added to the aqueous solution to perform a simulation experiment on the adsorption of phenolic pollutants in the actual water sample (Table S11, Fig. S11†).

2.7. Material characterization

¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra of TPPy were recorded by Bruker Avance spectrometer, and dissolved in CD₂Cl₂. The molecular weight of TPPy was determined by electrospray high resolution mass spectrometry(Bruker Impact II). Fourier-transform infrared (FTIR) spectra were recorded with a Bruker Tensor 27 spectrophotometer with a disc of KBr from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} . Solid-state ¹³C cross-polarization/magic-angle-spinning (CP/MAS) NMR and ²⁹Si MAS NMR spectra were performed with a Bruker Avance-500 NMR spectrometer operating at a magnetic field strength of 9.4 T. Nitrogen sorption isotherms were measured on a Micro Meritics surface area and pore size analyzer. The samples were degassed at 150 °C for 12 h prior to measurement. A sample of approximately 400 mg and a UHPgrade nitrogen (99.999%) gas source were used in the nitrogen sorption measurements at 77 K and collected on a Quantachrome Quadrasorb apparatus. The Brunauer-Emmett-Teller surface areas (BET) were investigated in the range $0.01 \le P/P_0 \le 0.2$. Pore size distributions were calculated using the Nonlinear Density Functional Theory (NL-DFT) kernel as implemented in the carbon/slit-cylindrical pore mode of the Quadrawin software. Powder X-ray diffraction (PXRD) were performed on a Riguku D/MAX 2550 diffractometer using Cu-K_a radiation at 40 kV and 200 mA with a scan rate of 10° min⁻¹. Thermal gravimetric analysis (TGA) was measured on a Mettler-Toledo SDTA-854 TGA system with heating rate of 10 $^\circ$ C min $^{-1}$ from room temperature to 800 $^\circ$ C in nitrogen atmosphere. High-resolution transmission electron microscopy (HR-TEM) experiments were recorded with a JEM 2100 electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. Field-emission scanning electron microscopy (FE-SEM) experiments were recorded with a HITACHI S4800 spectrometer. The luminescence excitation spectra were measured on Hitachi F-4500 fluorescence spectrophotometer equipment. The UV-Vis absorption spectrum was obtained by Cary 5000 UV-Vis Spectrophotometer.

3. Results and discussion

3.1. Characterization of PCS-TPPy

The synthesis of PCS-TPPy is successfully achieved by Friedel–Crafts reaction of OVS with TPPy (molar ratio of OVS to TPPy is 2:1) (Scheme



PCS-TPPy

1). Theorily, the starting molar ratio of reactants and the final molar ratio in the product should be same because the Friedel-Crafts reaction is a polyaddition reaction. According to the elemental analysis of the final product, the ratio of C:H is 10.04:1 (mass ratio), as shown in Table S4, which is a little lower than starting ratio of C:H (mass ratio is 11.68:1). This is probably ascribed to the enwrapped catalyst in PCS-TPPy. In order to explore the influence of molar ratio of OVS to TPPy on the porosity and fluorescent properties, we have prepared another two materials with the molar ratio of 1:1 and 3:1. The other two synthesized materials are named as PCS-TPPy-a (molar ratio of OVS to TPPy is 1:1) and PCS-TPPy-b (molar ratio of OVS to TPPy is 3:1), respectively.

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The identification of PCS-TPPy is characterized by FTIR, solid-state 13 C and 29 Si NMR spectroscopy. The FTIR absorption bands at 2960 cm⁻¹ and 1458 cm⁻¹ might be attributed to the stretching and bending vibrations of saturated C–H, indicating aliphatic methylene fragment was formed after the successful Friedel–Crafts reaction. Moreover, one recognizes the characteristic peaks of PCS-TPPy at 3034 cm⁻¹ (part of the remaining vinyl) and 1120 cm⁻¹ (Si–O–Si absorption peak) (Fig. S1†) [25,27].

The solid-state ¹³C NMR spectrum of PCS-TPPy along with OVS is shown in (Fig. 1). The signals from PCS-TPPy are located at 128.2 ppm and 138.2 ppm, which are considered to be the result of overlapping sp^2 carbon atoms originating from the aromatic rings of TPPy unit and unreacted vinyl groups. And the signals appearing at the aliphatic region (10-60 ppm) are due to the formation of Si-CH₂-CH₂- or Si-CH(CH₃) linkers between cage and TPPy after reaction. Two peaks appeared at 11.2 and 39.0 ppm, corresponding to the methylene carbons of Si-CH₂-CH₂-TPPy or Si-CH₂-CH₂-TPPy, respectively; the peaks at 49.0 and 12.8 ppm should be assigned to the methine carbon of Si-CH(CH₃)-TPPy and methyl carbon of Si-CH(CH₃)-TPPy, respectively. This result indicated that the generation of regioisomers occurred in the Friedel--Crafts reaction [28a]. In the solid-state ²⁹Si NMR spectrum of PCS-TPPy (Fig. 2), there were two peaks at -66.5 and -69.4 ppm, which were attributed to T₃ units newly formed after the Friedel–Crafts reaction and corresponded to Si-CH2-CH2-TPPy and Si-CH(CH3)-TPPy, respectively [26,27]. Compared with OVS, the smaller peak at -80.2 ppm was assigned toT₃ silicon linked with the unreacted vinyl, which also proved the incomplete reaction of vinyl in OVS due to steric hindrance. No T1 or T_2 peak was observed $[T_n = CSi (OSi)_n(OH)_{3-n}]$, indicating that the intact cage structure is retained in the process of Friedel-Crafts reaction [28b,42]. The results of FTIR, solid-state ¹³C and ²⁹Si NMR spectroscopy demonstrated that OVS reacted with 1,3,6,8-Tetraphenylpyrene successfully to produce PCS-TPPy through facile Friedel-Crafts reaction.

Similar to silsesquioxanes-based porous materials previously



Scheme 1. Synthetic route of PCS-TPPy.

Fig. 1. Solid-state ¹³C CP/MAS NMR spectra of PCS-TPPy and OVS.



Fig. 2. Solid-state ²⁹Si MAS NMR spectra of PCS-TPPy and OVS.

reported, the powder X ray diffraction profile of PCS-TPPy (Fig. S2†) showed a wide-range diffraction peak at approximate 20°, which was attributed to the Si–O–Si linkage [45], indicating that the hybrid material owned an amorphous characteristic. At the same time, the morphology of PCS-TPPy was further characterized by field emission scanning electron microscopy (FE-SEM) and high-resolution transmission microscopy (HR-TEM). From the FE-SEM and HR-TEM images, non-uniform nanopores can be observed and no long-range ordered nanostructure aggregates are formed (Fig. S3†, S4†), which is consistent with the characterization result of PXRD. These results comprehensively show that PCS-TPPy is an amorphous material [27,42].

Thermogravimetric analysis (TGA) is an important method to evaluate the thermal stability of porous polymers. One can see in Fig. S5†, compared with TPPy and OVS, PCS-TPPy shows a higher thermal stability. This can be attributed to the highly cross-linked network and the introduction of inorganic silica-like cage, which improve the pyrolysis temperature of organic moieties in the network.

3.2. Porosity of PCS-TPPys (PCS-TPPy, PCS-TPPy-a, PCS-TPPy-b)

In order to optimize the molar ratio of OVS to TPPy, 1:1, 2:1, and 3:1 were chosen to explore the influence of reactant ratio on the final property of the material. The porosities of PCS-TPPvs are measured by the N₂ adsorption-desorption experiment at 77 K. As presented in Fig. 3 and Fig. S6[†], at a lower P/P₀, the amount of N₂ adsorption increased rapidly, and with the increase of P/P₀, the adsorption capacity gradually slowed down. The apparent hysteresis in the desorption curve indicates the presence of microporous and mesoporous structures in PCS-TPPy [46]. The specific surface area of PCS-TPPy-a, PCS-TPPy, PCS-TPPy-b can be determined by the Brunauer-Emmet-Teller (BET) method to be 1564 m²/g, 1236 m²/g and 54 m²/g, respectively, and the corresponding micropore area is calculated as $348 \text{ m}^2/\text{g}$, $455 \text{ m}^2/\text{g}$, and 25 m^2/g by the t-plot method. The pore size distribution (PSDs) of PCS-TPPys is obtained by non-local density functional theory (NL-DFT) analysis. All porous materials showed similar pore-size distributions curves, for example, PCS-TPPy has bimodal pore structure of micropores centered at around 1.69 nm and mesopores centered at about 2.77 nm. The respective total pore volume (Vtotal) of PCS-TPPy-a, PCS-TPPy, PCS-TPPy-b was 1.16, 0.98 and 0.052 $\text{cm}^3 \text{ g}^{-1}$ and the ratio of the micropore volume (V_{micro}) to the V_{total} of PCS-TPPys was 0.13, 0.20, 0.21, respectively. They could be regarded as mesoporous materials. Usually, higher local crosslinking density will result in higher surface area and different molar ratio of OVS to TPPy could result in different local crosslinking-density. It was observed that the surface area decreases with increasing OVS loading and the lowest surface area of 54



Fig. 3. (a) N₂ adsorption-desorption isotherm of PCS-TPPy mearsured at 77 K (inset was the pore size distribution curve of the PCS-TPPy calculated by NL-DFT.) (b) N₂ adsorption-desorption isotherm of PCS-TPPy@BP mearsured at 77 K (inset was the pore size distribution curve of the PCS-TPPy@BP calculated by NL-DFT.).

 m^2/g was achieved due to the lower crosslink-density, as shown in Table S2. PCS-TPPy has the highest micropore specific surface area and micropore volume, although its total specific surface area is lower than PCS-TPPy-a. An increase in the molar ratio of OVS to TPPy means an increase in the reactive sites of TPPy, which will increase the local crosslink density and result in a higher surface area. However, a further increase in the molar ratio of OVS to TPPy greater than 2:1 will increase the number of unreacted vinyl groups due to steric effect [25], resulting in a high free volume of porous polymers and a reduced surface area. In addition, due to the average crosslink density between OVS and TPPy, inter-framework may occur and cause pore filling in the network, which also reduces the surface area of PCS-TPPy-b.

3.3. Luminescence properties

We also investigated the fluorescence changes of PCS-TPPys with different molar ratios of OVS to TPPy. Three hybrid polymers were investigated in 10 mL N,N-dimethylformamide (DMF), and the test conditions were 340 nm for excitation wavelength, 5 nm and 10 nm for excitation and emission slit. As shown in Fig. S7[†], it is observed that the fluorescence intensity increases with increasing OVS loading and the

fluorescence intensity reaches maximum when the molar ratio of OVS to TPPy is 3:1 (PCS-TPPy-b). This is because the introduction of more cubic cages greatly prevent π - π stacking of TPPy units and enhances fluorescence intensity. This further confirms the influence of OVS and TPPy content on the porosity and fluorescence properties of synthesized materials.

The strong fluorescence of PCS-TPPy prompted us to explore its application in metal ions detection. 3.0 mg PCS-TPPy was added to ethanol/water solution (volume ratio 1:1) in the presence of various cations and anions (cations: blank, Fe²⁺, Ca²⁺, Mg²⁺, Mn²⁺, Ni²⁺, Co²⁺, Cu²⁺, Sr²⁺ and Cd²⁺; anions: F⁻, Cl⁻, Br⁻, I⁻, PO₃³⁻, BF₄⁻, SO₄²⁻, HSO₃⁻ and PO₄³⁻). The concentration of all ions is 10⁻³ mol L⁻¹. As shown in Fig. 4, it is observed that PCS-TPPy shows strong detection sensitivity to Ru³⁺ and Fe³⁺. Moreover, the introduction of other metal ions or anions has basically no effect on the quenching behavior of Ru³⁺ and Fe³⁺.

Moreover, in order to investigate the effect of pH on the detection efficiency of PCS-TPPy. The BR buffer solution was chosen to explore the influence of pH changes on luminescence properties test. As shown in Fig. S8†, the pH barely influenced the detection efficiency over the pH range of 1–7 as evidenced by the negligible effect on the fluorescence intensity, which reveals that the detection of Ru^{3+} or Fe³⁺ is very stable. Therefore, we choose deionized water (neutral) to conduct subsequent luminescence properties test.

The UV absorption spectra of Ru^{3+} and Fe^{3+} show that both ions have a peak at ~220 nm with a broad shoulder at ~300 nm, which partially overlaps the excitation peak of PCS-TPPy at ~375 nm (Fig. S9†). Therefore, one can explain the quenching mechanism by the internal filtering effect (IFE) [47]. The excitation energy of PCS-TPPy can be transferred to Ru^{3+} or Fe^{3+} indicating that there is a competitive absorption between Ru^{3+} or Fe^{3+} and PCS-TPPy [48]. Moreover, compared with other metal ions, Ru^{3+} shows stronger UV absorption intensity in the range of 500–700 nm, which overlaps with the fluorescence emission peak of PCS-TPPy (560 nm), which shows energy transfer also takes place between the two units [7]. This is consistent with the result that Ru^{3+} has a better quenching effect on PCS-TPPy than other metal ions (including Fe^{3+}).

Same as selectivity, sensitivity to metal ions also plays an important role in the development of environmental science [49,50]. In order to further determine the effect of metal ion concentration on the fluorescence performance of PCS-TPPy, the fluorescence intensity in Ru³⁺ and Fe³⁺ solutions with different concentrations are measured. As shown in Fig. 5, with the concentration of Ru³⁺ and Fe³⁺ increasing, the fluorescence intensity of PCS-TPPy gradually decreases. When the concentration of Ru³⁺ and Fe³⁺ ions is 3×10^{-3} and 5×10^{-3} mol L⁻¹, respectively, the fluorescence of PCS-TPPy is completely quenched. Obviously, PCS-TPPy shows better fluorescence quenching sensitivity to Ru³⁺. This may be attributed to the fact that the Ru(III)/Ru(0) couple (0.4V) has a higher reduction potential than Fe(III)/Fe(0) couple (-0.036V) [51,52]. As shown in Fig. 6, PCS-TPPy had a good linear



Fig. 4. The fluorescence intensity ratio of PCS-TPPy in the presence of various metal ions and anions before and after the addition of ${\rm Ru}^{3+}$ and ${\rm Fe}^{3+}$.



Fig. 5. The fluorescence emission spectra of PCS-TPPy with different concentrations of Ru^{3+} and Fe^{3+} .



Fig. 6. The detection linearity of PCS-TPPy to Ru^{3+} and Fe^{3+} .

response to Ru^{3+} from 10 to 1000 μM with detection limit of 3.12 μM (S/N = 3), and the linear range equation was (I_0/I)-1 = 0.480C(10^{-4}) - 0.298 (R^2 = 0.9972). Also, PCS-TPPy displays selective fluorescent sensing for Fe^{3+} with a low detection limit of 6.78 μM over other metal ions with the linear response ranging from 10 to 1000 μM . And the equation was denoted as (I_0/I)-1 = 0.221C(10^{-4}) - 0.002 (R^2 = 0.9973) [53,54]. Therefore, the results can further confirm the high sensitivity of PCS-TPPy for Ru^{3+} and Fe^{3+}, especially for Ru^{3+}, which is comparable to some other similar sensors (Tables S5–S6).

Therefore, the mechanisms of fluorescent quenching behavior can be explained in detail as the followings: firstly, PCS-TPPy is considered to be electron-rich due to the presence of TPPy unit with π conjugation system and cage core with Si-O-Si linkage in the crosslinked network, while Ru³⁺ and Fe³⁺ are both electron-deficient, which is prone to electron transfer and causes fluorescence annihilation [52]; secondly, from the UV absorption spectra of PCS-TPPy and metal ions, one can see that except for Ru³⁺ and Fe³⁺, the UV absorption spectra of other metal ions also overlap with the excitation or emission spectra of PCS-TPPy to a certain extent (Fig. S9[†]). However, these metal ions cannot cause the annihilation of PCS-TPPy, which can be attributed to their lower standard reduction potential (Mg(II)/Mg(0) couple (-2.37V), Sr(II)/Sr(0) couple (-2.89V), Fe(II)/Fe(0) couple (-0.45V), Ca(II)/Ca(0) couple (-2.87V), Co(II)/Co(0) couple(-0.28V), Mn(II)/Mn(0) couple (-1.03V), Cu(II)/Cu(0) couple (0.34V), Cd(II)/Cd(0) couple (-0.40V), Ni(II)/Ni(0) couple (-0.25V)) [55,56]. Meanwhile, the fluorescence quenching effect of Ru³⁺ for PCS-TPPy is better than Fe³⁺, which may also be related to the higher standard reduction potential of the Ru(III)/Ru(0) couple [51, 52]. For Cu^{2+} with high standard electrode potential, it cannot quench the fluorescence of PCS-TPPy, which could be attributed to its larger diameter (Cu²⁺, 1.5 Å). The diameters of other metal ions are collected as follows: Ru^{3+} , 1.4 Å; Fe^{3+} , 1.1 Å; Mg^{2+} , 1.4 Å; Sr^{2+} , 2.4 Å; Fe^{2+} , 1.6 Å; Ca^{2+} , 2.0 Å; Co^{2+} , 1.3 Å; Mn^{2+} , 1.3 Å; Cd^{2+} , 1.4 Å; Ni^{2+} , 1.4 Å [55,56]. This is due to the extensive cross-linked structure and the twisted arrangement of the peripheral aromatic ring preventing the larger diameter metal ions from approaching PCS-TPPy [57]. In summary, internal filtering effect (IFE), electron transfer, energy transfer, reduction potential and diameter could be the main factors that induced the high selectivity to Ru³⁺ and Fe³⁺ by PCS-TPPy.

3.4. Adsorption of phenolic pollutants

Environmental pollution is an important problem that human is facing nowadays [58]. According to the United Nations' survey, billions of cubic meters of human-made sewage are discharged into seawater and rivers every year. Among these pollutants, very dangerous and toxic phenolic substances pose a huge threat to human health due to their good water solubility. Therefore, the removal of toxic phenolic pollutants from water is a very important issue [59,60]. Here, 4-bromo-phenol (BP), hydroquinone (HQ) and phenol (PH) were chosen to investigate the adsorption behaviors of PCS-TPPy for phenolic pollutants in this work.

The standard curves of three phenolic pollutants are shown in Fig. S13-S15†. In the adsorption experiment, the adsorption capacity of PCS-TPPy was detected by measuring the UV absorbance intensity changes of the filtrate of phenolic pollutants. Fig. 7 depicts the effect of different concentrations of BP, HQ, and PH on the equilibrium adsorption capacity (Qe). The results show that at low concentrations, the Qe growth rate is obvious, and as the concentration increases, the equilibrium adsorption capacity tends to be flat and reach a saturated state. It can be seen from the Fig. 7 that PCS-TPPy shows the highest adsorption capacity of 1.53 mmol g⁻¹ (265 mg g⁻¹) for BP, which is higher than other adsorbents reported (Table S7). And the adsorption capacities of PCS-TPPy for HQ and PH are 0.68 mmol g⁻¹ (75 mg g⁻¹) and 0.50 mmol g⁻¹ (47 mg g⁻¹), respectively.

The understanding of interaction mechanism can be achieved through comprehensive experimental observations and theoretical calculations. Adsorption performance is not only highly affected by a variety of weak molecular interactions (such as electrostatic interaction, hydrophobicity, hydrophilicity, hydrogen bonding and van der Waals interaction), but also by the inherent characteristics of various adsorbents (such as pore size, shape, molecular scale, crystallinity, modified functional groups) [61]. As we know, silsesquioxane-based hybrid porous materials can be used as excellent adsorbents, which has been confirmed by previous reports [62]. By analyzing the nitrogen adsorption-desorption isotherm of PCS-TPPy@BP, one can see that its specific surface area and total pore volume are significantly reduced compared with PCS-TPPy (Fig. 3b and Table S2). And the reduction of the mesopore area is more obvious than micropore area, which proves that the adsorption of phenols in the mesopores is more obvious [63]. Besides, we have compared the porosity of PCS-TPPy with other similar adsorbents and found that whether the specific surface area or the pore volume of PCS is larger than other adsorbents listed in Table S7[†]. This also explains the high adsorption capacity of PCS-TPPy for BP, HQ and BP, showing the importance of porosity in the adsorption activity. One can see that the molecular size of these three phenolic pollutants follows the order: HO > BP > PH (Table S8, Fig. S12†). The surface area of PCS-TPPy calculated as 1236 $m^2 g^{-1}$ (Table S1), provides sufficient storage space for the adsorption of phenolic pollutants. From the perspective of porosity, the pore volume (0.98 $\text{cm}^3 \text{g}^{-1}$) of PCS-TPPy is much bigger than the molecular structure size of these three phenolic



Fig. 7. Adsorption isotherms of BP, HQ and PH onto PCS-TPPy.

pollutants; hence the adsorbate can easily penetrate into the adsorbent [60]. It can be distinctly seen from the molecular structure that the two-dimensional dimensions of BP ($0.651 \text{ nm} \times 0.432 \text{ nm}$), HQ ($0.654 \text{ nm} \times 0.432 \text{ nm}$) and PH ($0.568 \text{ nm} \times 0.432 \text{ nm}$) are significantly smaller than that of the micropores (1.41 nm). Therefore, PCS-TPPy could offer an excellent adsorption capacity for phenolic pollutants.

In order to understand the difference in adsorption of BP, HQ and PH by PCS-TPPy in more detail, we have also compared the affinity of the three phenolic substances with water. The solubility of PH, HQ and BP in water are 83 g/L, 60 g/L, 14 g/L (20 °C), respectively [64], which is consistent with the difference in adsorption of BP, HQ and PH by PCS-TPPy. Meanwhile, the π - π interaction of phenolic substances with PCS-TPPy is another important factor for its good adsorption. The phenolic molecules could be adsorbed onto PCS-TPPy by π - π interaction [65], resulting in excellent adsorption capacities for three phenolic substances.

To further verify the adsorption mechanism, three common adsorption isotherms were selected to fit the data, namely Langmuir, Freundlich and Temkin equations [65,66]. The results are shown in Fig. S16-S18† and Table S9. The adsorption behaviour of PCS-TPPy on these three phenolic pollutants is more in line with the Langmuir model, and its linear correlation coefficients (R_L^2) are 0.9799 (BH), 0.9249 (HQ) and 0.9557 (PH), respectively, which are significantly higher than Freundlich's R_F^2 and Temkin R_T^2 , indicating that the adsorption behaviour of PCS-TPPy on the three phenolic pollutants is close to monolayer and relatively uniform adsorption. According to theoretical calculations, the maximum adsorption capacity of PCS-TPPy for BP, HQ and PH is 1.88 mmol g⁻¹ (324.7 mg g⁻¹), 0.86 mmol g⁻¹ (94.87 mg g⁻¹) and 0.71 mmol g⁻¹ (67.25 mg g⁻¹), respectively, which is slightly higher than the corresponding experimental Qe value.

In view of the highest adsorption capacity of PCS-TPPy on BP, BP was chosen to explore the adsorption kinetics with an initial concentration of 30 mg L^{-1} . Fig. 8 depicts the effect of contact time on the absorption of BP by PCS-TPPy. One can see that the adsorption rate of PCS-TPPy is extremely fast and the system can reach adsorption equilibrium in 1 h.

In order to further explore the kinetic adsorption behavior of PCS-TPPy on BP [67–68], two common models were used for simulation. As shown in Fig. S19† and Table S10, R_2^2 (0.9992) of the pseudo-second-order kinetic model is higher than R_1^2 (0.9658) of the pseudo-first-order kinetic model; and the fitted equilibrium adsorption value (63.86 mg g⁻¹) is basically consistent with the experimental value (64 mg g⁻¹), which proves that the adsorption of BP by PCS-TPPy is more in line with the pseudo-second-order kinetic model.

Simultaneously, the regeneration and circulation of the adsorbent

were simulated to evaluate the reusability and stability of PCS-TPPy as an adsorbent. PCS-TPPy is added to an aqueous solution of phenolic pollutants (BP) with an initial concentration of 30 mg L⁻¹. The adsorbed material is repeatedly washed with ethanol and dichloromethane successively, and can be used after drying. Fascinatingly, it can be seen from Fig. 9 that even after 5 cycles of experiments, PCS-TPPy still maintains an ultra-high removal efficiency.

3.5. Adsorption of phenolic pollutants in real water samples

The detection and adsorption experiments were carried out by applying PCS-TPPy in three different types of water (lake water of Daming Lake, spring water of Black Tiger Spring and pool water of Five Dragons Pool in Jinan, China) with different concentrations of metal ions (Ru³⁺, Fe³⁺) or phenolic pollutants (BP, HQ, PH). As shown in Fig. S10^{\dagger}, after adding PCS-TPPy and a certain concentration (10⁻³ mol L^{-1}) of metal ions to different real water samples, one can see that even in different actual water samples, PCS-TPPy can still effectively detect Ru³⁺ and Fe³⁺. Moreover, after three certain molar amounts of phenolic pollutants were added to the three actual water samples, and then PCS-TPPy was added to the aqueous solution to perform a simulation experiment on the adsorption of phenolic pollutants in the actual water samples (Table S11, Fig. S11⁺). And the results show that PCS-TPPy has a slightly lower equilibrium adsorption capacity (Qe) for phenolic pollutants than corresponding value under the same conditions in the deionized water. This may be related to the natural organic matter (NOM) that has similar structure to phenolic pollutants in actual water samples, which may have effects on the adsorption performance for the phenolic pollutants [10]. Besides, the adsorption behaviour of PCS-TPPy to these three phenolic pollutants in real water samples is also more in line with the Langmuir model, indicating that the adsorption behaviour of PCS-TPPy on the three phenolic pollutants is indeed close to monolayer and relatively uniform adsorption.

4. Conclusion

In summary, we use octavinylsilsesquioxane (OVS) and tetraphenylpyrene (TPPy) as reaction units to successfully prepare silsesquioxane-based hybrid fluorescent porous polymer (PCS-TPPy) through efficient and concise Friedel-Crafts reaction. The resulting polymer shows a high surface area of 1236 m² g⁻¹, total pore volume of 0.98 cm³ g⁻¹, and hierarchical structure with micropores and mesopores. The excellent fluorescence of PCS-TPPy makes it to selectively detect Ru³⁺ and Fe³⁺ with good linear response from 10 to 1000 μ M and the corresponding detection limits are 3.12 μ M and 6.78 μ M,



Fig. 8. Effect of contact time on the absorption of BP by PCS-TPPy.



Fig. 9. The removal efficiency of PCS-TPPy for BP after five cycles.

respectively. Moreover, the high surface area, hierarchical microporous/mesoporous structure and conjugated structure of tetraphenylpyrene linker in this material make it to favor phenolic pollutants adsorption with an excellent adsorption capacity of 1.53 mmol g⁻¹ for 4-bromo-phenol (BP), 0.68 mmol g⁻¹ for hydroquinone (HQ) and 0.50 mmol g⁻¹ for phenol (PH), respectively. Importantly, PCS-TPPy exhibits excellent regeneration performance. This discovery shows that silsesquioxane-based porous polymers have broad prospects in environmental field and may generate new insights in practical applications.

Credit author statement

Prof. Hongzhi Liu offers the idea of this paper and revises the paper. Nan Yang does experiments and writes the draft of this paper.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (No. 21975144), Key Research and Development Program of Shandong Province (2019GHZ034) and Seed Fund Program for the International Research Cooperation of Shandong University.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2021.124083.

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