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Supporting Information

ABSTRACT: A layer of synthetic supramolecular macrocycles, that is, perhydroxyl-pillar[5]arene and perhydroxyl-pillar[6]arene, has been covalently attached to hydrophilic silica supports through Si−O−Si linkages with a coverage of up to 250 μmol pillar[5,6]arenes/g to form novel absorbent hybrid materials. Their adsorption toward a typical herbicide, namely, paraquat, from its aqueous solution has been investigated. Kinetic studies disclosed that paraquat adsorption fits a first-order kinetic model. Equilibrium adsorption data could be explained very well by the Langmuir equation. The pillar[6]arene-modified materials showed more obvious adsorption as compared with pillar[5]arene-modified ones and the saturation adsorption quantity reached about 0.20 mmol of paraquat per gram of materials. The entire process of adsorption was endothermic, and significantly an elevated temperature led to an increase in the adsorption quantity. This new type of pillarene-based adsorbent materials can be considered as a potential adsorbent for harmful substances removal from wastewaters.

INTRODUCTION

Herbicides have been used in agriculture for over two hundred years. Nowadays, many herbicides are approved for use as nonsystemic contact herbicides for green vegetation, such as paraquat, contributing significantly to advance modern agriculture.1 However, due to the extensive use of a wide range of chemicals in modern agriculture, the preconcentration and removal of pesticides become extremely important for environmental control and human health.2

This has aroused much interest in using supramolecular macrocycles with intrinsic cavities as desirable hosts for the specific adsorption of small molecular targets. In this regard, organic supramolecular chemistry has afforded important possibilities for the preparation of new adsorbents and extraction reagents, especially with the progress of synthetic macrocyclic receptors,3 for example, crown ethers,4 calixarenes,5−7 cyclodextrins,8−11 and cucurbiturils.12 However, as a newly developed member of synthetic macrocycles, pillarenes are rarely studied as adsorbents functionalized on solid supports.

The pillared structure and easy modification of pillarenes have provided them outstanding capability to complex different types of guests (from charged molecules, i.e., cations and anions, to neutral compounds) selectively13−15 and afforded a valuable platform for the construction of numerous interesting supramolecular systems, for example, virus inhibitors,16 chemical sensors,17−19 supramolecular polymers,20−25 artificial transmembrane channels,26,27 hybrid nanomaterials,28−30 drug delivery and controlled release systems,31,32 molecular machinery,33−36 metal−organic frameworks,37−45 and so forth.46−49

Herein, we immobilized pillar[5,6]arenes (P5 and P6), consisting of 10 or 12 phenol hydroxyl groups, onto the chlorinated surface of silica supports, for the first time, to form organic−inorganic hybrid materials, that is, P5−Si and P6−Si, possessing specific adsorption capability toward paraquat based on the host−guest inclusion complexation (Scheme 1). In this article, we wish to present the synthesis, characterization, and adsorption analysis of two adsorbents comprising hydroxyl pillarenes functionalized directly onto the surfaces of chlorinated silica. The surface-functionalization method is applicable to other pillarene derivatives to obtain new materials with immobilized pillarenes rigidly on a silica oxide surface, holding great potential in fundamental studies and industrial applications, such as guest adsorption, sensing, and catalysis. Meanwhile, by studying the dynamic behavior of paraquat adsorption from an aqueous solution onto the solid materials, one obtains information about the complexation performance of pillarenes toward analytes in aqueous solutions, where bulk pillarenes without additional modification are generally poorly soluble.

EXPERIMENTAL METHODS

Synthesis. All reagents were commercially available. Silica (1−100 μm of primary particle size), triethylamine, and SiCl4 were reagent grade, which was obtained from Aladdin Reagents. Deionized water...
was employed in all experiments unless otherwise noted. 1,1'-Dimethyl-4,4'-bipyridinium salt (paraquat) was prepared according to the literature report. The P5 (MW = 610 g/mol) and the P6 (MW = 732 g/mol) used in the materials were synthesized based on methods in the literature.

Our method for pillarene immobilization on silica is inspired by calixarene immobilization, which relies on stable direct linkages between phenolic oxygens or hydroxyl on the lower rim of calixarene and a silicon atom on silica surface via organic chlorosilane reaction. First, we employed SiCl₄ to react with silanol groups and a silicon atom on silica surface under anhydrous conditions so that a layer of O-SiCl₃ species can be immobilized on the interior surface of silica. The activated silica surface can then further react with perhydroxyl-pillarene under the presence of a representative base, for example, triethylamine, resulting in covalent immobilization of pillarenes onto silica supports (Scheme 2).

In the reaction, triethylamine and PhMe were newly distilled from CaH₂ with N₂ protection before use. The silica starting material (1.2 g) was dehydrated at 250 °C under a dynamic vacuum of >50 mTorr for 2 days and then cooled down to room temperature under N₂. By standard air-free techniques, a solution of SiCl₄ in CH₂Cl₂ (1 M, 6.8 mL) was added into the reaction system via a dry syringe, followed by the addition of triethylamine (0.69 g, 6.8 mmol). Then, the flask was sealed under N₂ and was shaken at 200 rpm for 1 day at rt, followed by the subsequent evaporation of solvents in vacuo to yield a white powder. This powder was then dried under a dynamic vacuum for 1 day to result in chlorinated silica material. Thereafter, a solution of the macrocycle P5 (0.305 g, 0.50 mmol) or P6 (0.360 g, 0.50 mmol) in PhMe (15 mL) was readily prepared, and the powder (1 g) was added followed by the repeated rinse of the flask with PhMe (10 mL). At last, triethylamine (1.75 g, 17.3 mmol) was injected to the reaction mixture, which was further heated at reflux under N₂ for more than 1 day. The reaction was run in a heterogeneous system. Materials were then filtered off and washed sequentially with boiling PhMe (100 mL), methanol (50 mL), deionized water (50 mL), methanol (50 mL), acetone (100 mL), and petroleum ether (30 mL). The obtained powder was then dried in ambient air, followed by Soxhlet extraction for 1 day with anhydrous hot benzene and vacuum drying at room temperature for 1 day.

**Characterization.** FT-IR spectra were obtained on a Bruker Vertex 80 V. Thermogravimetric analysis (TGA) was performed on a TGA Q500 instrument operated in a high-resolution mode with a temperature ramp of 10 °C/min to 800 °C under a dry air flow in an alumina pan. Diffuse reflectance UV–vis spectra were recorded with a Lambda 950 UV–vis spectrophotometer coupled with a Harrick praying mantis diffuse-reflectance accessory. Ultraviolet–visible (UV–vis) spectroscopy was measured on a Shimadzu UV-2550 instrument.

**Adsorption Experiment.** To investigate the adsorption kinetic behavior of paraquat onto adsorbent, a conventional batch adsorption approach was employed by preparing paraquat solution (0.01–0.25 mM, 5 mL) with fresh adsorption materials (P5–Si, P6–Si, and SiO₂) (5–10 mg) in glass bottles sitting in a laboratory shaker at 200 rpm and a stable temperature. At different paraquat adsorption times, the paraquat solution was separated from the adsorbent by centrifugation (10 000 rpm, 5 min). By checking the solution residual paraquat at a maximum absorption wavelength (257 nm) on a UV–vis spectrophotometer, the paraquat adsorption amount on the materials at different times was assessed.

Adsorption isotherms were then acquired at different paraquat adsorption times, the paraquat solution was separated from the adsorbent by centrifugation (10 000 rpm, 5 min). By checking the solution residual paraquat at a maximum absorption wavelength (257 nm) on a UV–vis spectrophotometer, the paraquat adsorption amount on the materials at different times was assessed.

Adsorption isotherms were then acquired at different temperatures with the employment of a batch equilibration technique. The samples were further equilibrated for 1 day at 200 rpm on a laboratory shaker.

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**RESULTS AND DISCUSSION**

**Characterization.** Figure 1 shows a representative weight loss curve of TGA. The weight loss of silica (Figure 1, curve a) was ca. 0.3%, resulting from the loss of water in the temperature interval of physisorbed water. Thermogravimetric analysis of pure pillarene (Figure 1, curve c) showed a rapid weight loss of solvents (5%) up to 220 °C, followed by a plateau until 370 °C,
where decomposition of compound began. For the hybrid materials (Figure 1, curve b), the first step of weight loss can be ascribed to the loss of water and the solvent desorption from the solid materials, and based on curve c in Figure 1, the second weight loss step was ascribed to pillarene decomposition. To determine pillarene loading, curve of weight loss was therefore normalized by the weight at 220°C and the curve of pure silica was subtracted. The loading of pillarenes is about 18%. So the coverage is about 0.25 mmol pillarenes/g, which is close to the number calculated from elemental analysis (Table S1 in the Supporting Information (SI)).

The FT-IR spectra of silica (curve a), hybrid materials (curve b), and pillarenes (curve c) were recorded by FT-IR spectrometry as shown in Figure 2. The band at 3337 cm⁻¹ in the FT-IR spectrum of silica in Figure 2a was assigned to the vibration of –OH stretching. The band at 1091 cm⁻¹ could be the asymmetrical stretching of silicon oxy tetrahedron. The bands at 803 cm⁻¹ and 488 cm⁻¹ corresponded to the symmetrical stretching and bending of Si–O, respectively. For pillarenes, the vibrations of ring moiety at 783 cm⁻¹ and 921 cm⁻¹, the phenyl plane bending at 1500 cm⁻¹, CH₂ stretching at 2930 cm⁻¹, and C–H/O–H bending at 1416 cm⁻¹ could be clearly seen in Figure 2c. As shown in Figure 2b, the bands observed at 1500 cm⁻¹ and 2930 cm⁻¹ were ascribed to phenyl vibrations and CH₂ stretching vibrations, respectively, indicating that pillarenes were successfully modified on silica surface.

Characteristic diffuse reflectance UV–vis spectra have been provided in Figure 3 for pure silica (curve a), hybrid materials (curve b), and pure powdered pillarene (curve c). The peak at ca. 280 nm was characteristic of aromatic core of pillarenes. After pillarene grafting, the hybrid materials also showed the characteristic peaks of pillarenes. From these analyses, we can conclude that the pillarene macrocycles have been successfully grafted onto the surface of silica dioxide for the first time. From the SEM micrograph of SiO₂ and P₅–Si (Figure S7 in the SI), it was clear that the morphology of silica has no change after pillar[5]arene’s modification on silica surfaces.

**Batch Experiments.** The adsorptive capability of the hybrid materials toward herbicide in an aqueous solution was examined, using paraquat as a typical herbicide. The equilibrium adsorption amount of paraquat, qₑ (mmol/g), can be calculated using the following relationship

$$q_e = \frac{(c_0 - c_e)V}{W}$$

Here, $c_0$ (mmol/L) is the initial adsorbate concentration, $c_e$ (mmol/L) is the equilibrium concentration of paraquat, and $V$ (L) is the adsorbate volume at any time.

**Kinetic Behavior of Adsorption.** Based on batch adsorption experiments at different temperatures, the quantities of paraquat adsorbed at different times are depicted in Figure 4. The concentration of paraquat was held constant. The adsorbed amount of paraquat increased upon increasing contact time and reached equilibrium for P₅–Si after 80 min (Figure 4A). When P₆–Si was employed as adsorbent, the paraquat adsorption quantity increased rapidly with time during the first 20 min, and after 60 min adsorption equilibrium was reached as can be seen in Figure 4C.

In order to rule out the order of adsorption kinetics, the equation of first-order kinetics was first examined. The time-dependent paraquat adsorption quantity can be calculated as follows.
Here, $k_s$ (min$^{-1}$) is the adsorption rate constant and $q_e$ (mmol/g) and $q_t$ (mmol/g) are adsorption quantity of adsorbed paraquat at equilibrium and at any time, respectively. The linearity between $-\ln\left(1 - \frac{q_t}{q_e}\right)$ and $t$ shows that the adsorption of paraquat onto the materials was a pseudo-first-order reaction (Figure 4B and D). According to the slope of the straight lines of the plot, the rate parameters $k_s$ and $q_e$ at different temperatures can be easily attained from the intercept and the slope. Rate parameter $k_s$ was tested as listed in Table 1. 

The Arrhenius equation should be used to define the relationship of the pseudo-first-order rate constant $k_s$ with temperature $T$ as follows

$$-\ln\left(1 - \frac{q_t}{q_e}\right) = k_s t$$

Here, $E_a$ (kJ/mol) represents the apparent activation energy; $R$ represents the gas constant; and $A$ represents the apparent pre-exponential factor. Relationship between $\ln k_s$ and $T^{-1}$ is provided in Figure 5. The apparent activation energy, $E_a$, was assessed from the slope of the straight line, which is shown in Table 1. The value of apparent activation energy $E_a$ of P6–Si is smaller than P5–Si, indicating that the adsorption reaction of paraquat onto P6–Si was easier than that of P5–Si. This is in accordance with the larger value of the $k_s$ and $q_e$ of P6–Si and the higher binding constant between P6 and paraquat.47,48

**Adsorption Isotherms.** The adsorption isotherm is describing the relationship between adsorbate and adsorbent. In this article, the sorption equilibrium isotherms were measured at 25, 30, 35, 40, and 45 °C, as shown in Figure 6A and C. From the results, the adsorption capacity of adsorbents was found to be increased with an increasing initial

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**Table 1. Equilibrium Adsorption Quantity, $q_e$, the Pseudo-First-Order Rate Constant, $k_s$, and the Apparent Activation Energy, $E_a$, at Different Temperatures**

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>P5–Si</th>
<th>P6–Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298</td>
<td>303</td>
</tr>
<tr>
<td>$q_e$ (mmol/g)</td>
<td>0.025</td>
<td>0.026</td>
</tr>
<tr>
<td>$k_s$ (min$^{-1}$)</td>
<td>0.017</td>
<td>0.023</td>
</tr>
<tr>
<td>$E_a$ (kJ/mol)</td>
<td>16.0</td>
<td></td>
</tr>
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</table>

$\ln k_s = -\frac{E_a}{RT} + \ln A$

**Figure 4.** Relationship between $q_t$ and $t$. (A) P5–Si, (C) P6–Si. The plot of $-\ln\left(1 - \frac{q_t}{q_e}\right)$ versus $t$. (B) P5–Si, (D) P6–Si. Temperature, °C: ■, 25; ●, 30; ▲, 35; ▼, 40; ◆, 45.
concentration of paraquat in solution and the adsorption capacity of P6-Si is better as compared with that of P5-Si.

Langmuir and Freundlich adsorption models have generally been used to study the adsorption phenomenon. The background adsorption amount of paraquat onto silica support without pillarenes was less than 5% of the adsorption to materials under the same conditions. The adsorption may primarily be attributed to inclusion complexes formed between pillarene and paraquat. So, assuming that the adsorption coincided with Langmuir model, the most widely used two-parameter equation can be represented as

$$\theta = \frac{q_e}{q_m} = \frac{K_L c_e}{1 + K_L c_e}$$

where $\theta$ represents the fractional coverage and $q_m$ represents the amount adsorbed per unit mass of adsorbent corresponding to complete coverage. $K_L$ (L/mmol) is the Langmuir constant. Rearranging the equation above, we can reach

$$\frac{c_e}{q_e} = \frac{c_e}{q_m} + \frac{1}{K_L q_m}$$

The relationships between $c_e/q_e$ and $c_e$ at different temperatures were presented in Figure 6B and D. Linear relationships can be observed, implying that the adsorption of paraquat onto silica support obeyed Langmuir’s model. In addition, the interactions of pillarene with paraquat were previously investigated in acetone, exhibiting a good binding affinity. The results implied that pillarene could provide specific adsorption sites for paraquat. Upon increasing temperature, the parameters of $q_m$ and $K_L$ gradually increase (Table 2), also implying that the higher the temperature in our selected

**Figure 5.** Relationship between ln $k_s$ and $T^{-1}$. (a) P5-Si and (b) P6-Si.

**Figure 6.** Adsorption isotherm for paraquat onto the hybrid material adsorbents. (A) P5-Si and (C) P6-Si. Relationship between $c_e/q_e$ and $c_e$ at different temperatures. (B) P5-Si and (D) P6-Si. Temperature, °C: ■, 25; ●, 30; ▲, 35; ▼, 40; ◆, 45.
Table 2. Saturation Adsorption Quantity, $q_m$, Adsorption Constant, $K_L$, and Separation Factor, $R_L$, for the Langmuir Isotherm at Different Temperature

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>P5–Si</th>
<th>P6–Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$ (mmol/g)</td>
<td>$K_L$ (L/mg)</td>
</tr>
<tr>
<td></td>
<td>0.088</td>
<td>173.4</td>
</tr>
<tr>
<td></td>
<td>0.092</td>
<td>179.5</td>
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<tr>
<td></td>
<td>0.105</td>
<td>179.7</td>
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<tr>
<td></td>
<td>0.118</td>
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<td></td>
<td>0.123</td>
<td>221.0</td>
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<tr>
<td>329.2</td>
<td>0.196</td>
<td>0.207</td>
</tr>
<tr>
<td>366.7</td>
<td>0.222</td>
<td>0.235</td>
</tr>
<tr>
<td>398.2</td>
<td>0.352</td>
<td>0.366</td>
</tr>
<tr>
<td>400.8</td>
<td>0.400</td>
<td>0.425</td>
</tr>
<tr>
<td>428.5</td>
<td>0.428</td>
<td>0.428</td>
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</table>

Table 3. Thermodynamic Parameters of Paraquat Adsorption on Adsorbent at 298.15 K

<table>
<thead>
<tr>
<th></th>
<th>P5–Si</th>
<th>P6–Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H^0$ (kJ/mol)</td>
<td>7.44</td>
<td>9.7</td>
</tr>
<tr>
<td>$\Delta S^0$ (J/k/mol)</td>
<td>73.72</td>
<td>75.04</td>
</tr>
<tr>
<td>$\Delta G^0$ (kJ/mol)</td>
<td>$-14.54$</td>
<td>$-12.67$</td>
</tr>
</tbody>
</table>

The analysis above and the positive enthalpy changes (Table 3) suggested a slightly endothermic nature for paraquat adsorption. On the whole, the adsorption quantity always decreases upon increasing temperature, but the uncommon behavior may be attributed to desolvation. The adsorption of paraquat onto materials was an exothermic reaction. However, the desorption heat of high-energy solvents from the cavity of pillarenes was bigger than the heat of paraquat adsorption onto silica. Thus, the whole adsorption process was endothermic. Moreover, using the positive value of the entropy change ($\Delta S^0$), the adsorption at the pillarene site has favorable entropy of adsorption of about 74 J/mol/K. The adsorption was driven by entropic increase. Because of the poor solubility of perhydroxyl-pillarenes in aqueous solution, little has been discovered about their complexation toward guests in an aqueous solution, but the complexation of pillarene and paraquat in organic solvents has been verified by Ogoshi and Huang et al. So, the complexation was driven by desolvation and hydrogen-bonding effect in the inclusion complexation of paraquat and silica surface-bonded pillarenes.

**CONCLUSIONS**

In summary, pillarenes have been directly grafted onto silica surfaces, fully characterized, and employed in the paraquat adsorption from dilute aqueous solutions based on their inclusion complexation for the first time. These research results suggested the potential application of pillarene–silica hybrid materials for the separation of harmful substances from the water aqueous phase. Finally, the synthetic protocols presented herein can be used and expanded to an extensive class of functionalized pillarenes and different kinds of solid supports, which may provide a better understanding of pillarene–guest chemistry and lead to new, selective adsorbents in the future.
■ REFERENCES


(50) Delageix, X.; Hosseini, M. W. Multicavatans III: Synthesis and NMR Studies of a Tri-directional Koiland Composed of Three p-tert-