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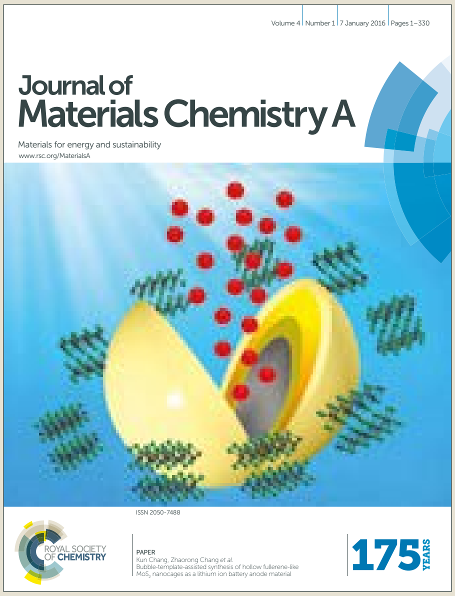

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COMMUNICATION

Pillar[n]arene based porous polymers for rapid pollutant removal from water

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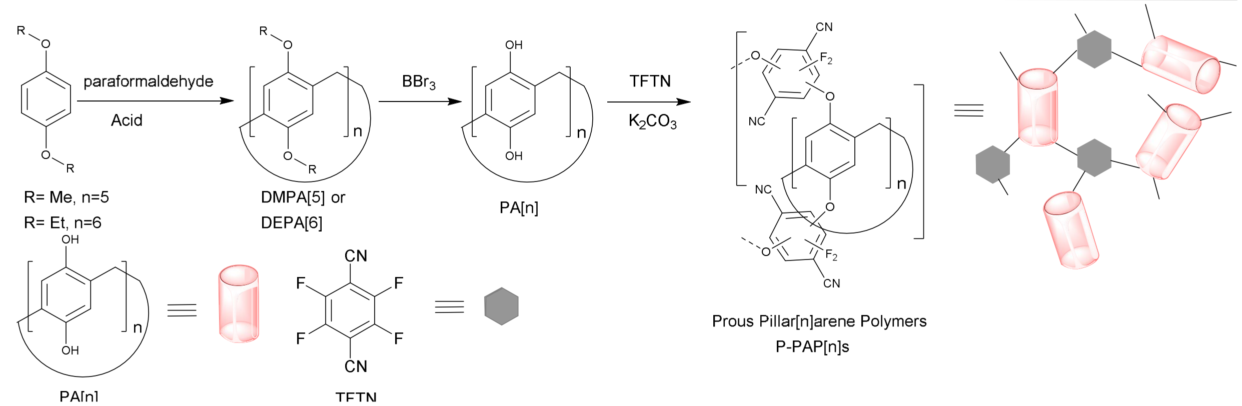
Pillar[n]arene (PA[n], n = 5 or 6) based porous polymers (P-PAP[n]s) were prepared by crosslinking PA[n]s, and used as adsorbents to remove pollutants from water via host-guest interactions. These new materials are adsorbents for a wide range of contaminants with fast removal kinetics. The adsorption is especially efficient for herbicide paraquat with a very fast uptake kinetics (k_2 = 33.3 g mg^{-1} min^{-1}, at least 5 times faster than any existing adsorbent for paraquat) and a high removal capacity (209 mg g^{-1}).

Water pollution is a global environmental problem threatening aquatic ecosystem and human health. Paraquat (1,1'-dimethyl-4,4'-bipyridynium dichloride), widely used as a non-selective herbicide and the active ingredient of Gramoxone, is an important hydrophilic pollutant.[1] As a highly toxic chemical, residual paraquat in water, soil and food could cause severe health and environmental hazards.[2–4] To remove paraquat, adsorption with porous materials has been extensively investigated due to its simplicity, high efficiency and low operational cost.[5–9] However, the performance of existing adsorbents is not satisfactory, suffering from slow uptake kinetics and limited removal capacity.



Scheme 1 Syntheses of porous PA[n] polymers.

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Electronic Supplementary Information (ESI) available: general experimental, synthetic procedures, characterizations of P-PAP[6], UV-Vis spectra of pollutant removal experiments, and the comparison of paraquat removal performance with different adsorbents. See DOI: 10.1039/x0xx00000x

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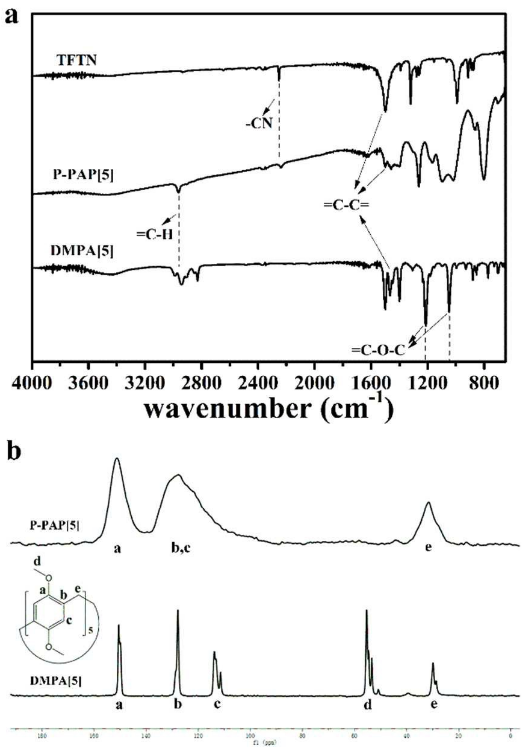


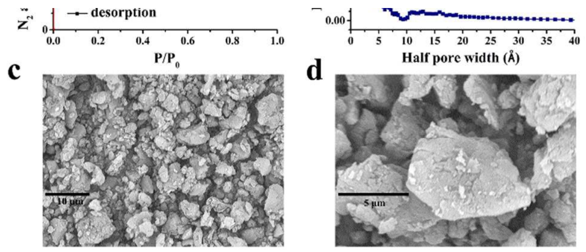
Since the discovery by Ogoshi and co-workers in 2008, pillar[n]arenes (PA[n]s, n = 5-10) have emerged as a new type of macrocyclic hosts with remarkable host-guest recognition property and promising applications.[10,11] The unique pillar-shape architectures and rigid π-rich cavities of PA[n]s make them high affinity hosts for paraquat and other electron deficient molecules.[12] Syntheses of PA[n]s start from inexpensive compounds, and preparations for PA[5] and PA[6] are facile.[13] With low synthetic costs and excellent recognition properties, PA[5] and PA[6] are ideal building blocks to construct functional materials. PA[n]s have been used to prepare polymeric materials,[14,15] metal-organic frameworks (MOFs),[16] supramolecular-organic frameworks (SOFs) ,[17] hybrid materials,[18] self-assembly materials[19,20] and 2-D materials.[21] These PA[n] based materials are used for artificial transmembrane channels,[22] drug delivery,[23] light harvesting,[24] and chemical separation.[25,26] New PA[n] based materials are of great interests to help tackle health, energy and environmental challenges.

Fig. 1 (a) FT-IR spectra of TFTN, P-PAP[5] and DMPA[5]. (b) Solid-state ^{13}C NMR spectra of P-PAP[5] and DMPA[5].

Herein, we report PA[n] based porous polymers, which can uptake a variety of pollutants from water with fast kinetics. These adsorbents are especially efficient for paraquat with a very fast uptake rate and high adsorption capacity. Their excellent pollutant removal ability makes these polymers promising adsorbents for waste-water treatment.

We chose PA[5] (DMPA[5]) and PA[6] (DEPA[6]) as starting materials to prepare porous polymers. PA[5] and PA[6] are important members of PA[n] family, and their syntheses are relatively simple. The preparation of PA[5] is especially facile. The acid catalysed condensation reaction delivers DMPA[5] as a single major product with a high yield of 70%,[27] which makes the large scale synthesis and practical applications possible. The synthetic procedures of PA[n] based polymers are depicted in Scheme 1.[13,28] The alkyl groups on DMPA[5] and DEPA[6] were removed with BBr_3.[10] After washing, phenolic hydroxyl bearing PA[n]s were crosslinked by tetrafluoroterephthalonitrile (TFTN) in a suspension of K_2CO_3 in DMF at 90 ℃, following methods reported by Dichtel and co-workers.[29] The crosslinking reaction is a nucleophilic substitution reaction of phenolic hydroxyl groups to replace fluoride on TFTN. PA[n] based polymers precipitated out of the reaction solution, and were used after filtration and washing with a yield of 48% for P-PAP[5] and 20% for P-PAP[6].

Fig. 2 (a) N_2 adsorption isotherms of P-PAP[5]; (b) the cumulative pore volume (half pore width) of P-PAP[5] obtained by non-local density functional theory (NLDFT) analysis; (c) and (d) SEM images of P-PAP[5]. Scale bars represent 10 μm (c) and 5 μm (d), respectively.



The molecular structures of P-PAP[n]s were elucidated with FT-IR and solid-state ^{13}C-NMR. The FT-IR spectra of DMPA[5], TFTN and P-PAP[5] are shown in Fig. 1a. The FT-IR spectrum of TFTN shows absorbance at 2252 cm^{-1}, corresponding to the nitrile stretch. The FT-IR spectrum of DMPA[5] has absorbance at 2941cm^{-1}, corresponding to the aromatic C-H stretch. Both resonances are present in the FT-IR spectrum of P-PAP[5], which is evident for the incorporation of PA[5] and TFTN moieties. The aliphatic C-O-C stretch peaks at 1048 cm^{-1} and 1242 cm^{-1}, found in the FT-IR spectrum of DMPA[5], are absent in the FT-IR spectrum of P-PAP[5], indicating the removal of methyl groups in PA[5] and the crosslinking via TFTN aromatic moieties. The formation of P-PAP[5] was further verified with solid-state ^{13}C-NMR (Fig. 1b). The ^{13}C-NMR spectrum of DMPA[5] exhibits resonances at 150 ppm, 127 ppm and 113 ppm, corresponding to sp^2 carbons of the phenyl rings. The corresponding broadened resonances are observed in the ^{13}C-NMR spectrum of P-PAP[5]. The resonance peak at 30 ppm corresponding to the methylene carbons of PA[5] is found in both spectra. These observations confirm the PA[5] moiety in P-PAP[5]. The peak at 55 ppm in the spectrum of DMPA[5], corresponding to methyl carbons, is not found in the spectrum of P-PAP[5], which indicates the removal of methyl groups.

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Similar observations are identified in the FT-IR and solid-state ^{13}C-NMR spectra for P-PAP[6] (Fig. S1 and S2).

Nitrogen adsorption isotherms of P-PAP[5] (Fig. 2a) and P-PAP[6] (Fig. S3a) are Type Ⅰ, demonstrating the existence of micropore in the polymers. The Brunauer-Emmett-Teller (BET) specific surface areas are calculated to be 529 m^2 g^{-1} for P-PAP[5], and 533 m^2 g^{-1} for P-PAP[6]. The large BET specific surface areas show that these materials are highly porous. The cumulative pore volume curve of P-PAP[5] demonstrates large portions of the half pore width are below 5 Å (Fig. 2b), corresponding to the half width of PA[5] cavity (2.8 Å).[30] These polymeric materials have a medium size of ~8 µm, as observed in SEM images (Fig. 2c-d). Their porosity and micrometer sizes make them ideal candidates as adsorbents.

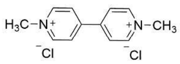
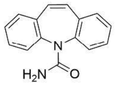
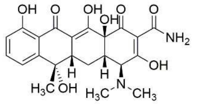
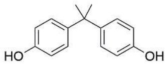
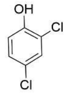
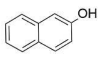
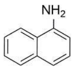
	Paraquat	Cu^{2+}	carbamazepine	tetracycline	BPA	2,4-DCP	2-NO	1-NA
								
P-PAP[5]	97%	88%	90%	66%	96%	82%	87%	82%
P-PAP[6]	96%	93%	96%	76%	98%	79%	96%	84%
AC	13%	16%	84%	36%	96%	86%	80%	77%
P-CDP	—	—	—	—	80%	72%	78%	82%

Table 1 Flow-through adsoprtion efficiency of P-PAP[5], P-PAP[6], activated carbon (AC, Norit® SA 2) and P-CDP for various pollutants.

We moved on to investigate the application for pollutant removal from water. We chose pollutants spanning herbicide (paraquat), heavy metal (Cu^{2+}), pharmaceutical compound (carbamazepine), antibiotic agent (tetracycline), plastic component (bisphenol A), and simple aromatics (1-naphthyl amine, 2,4-dichlorophenol, 2-naphthol). These contaminants belong to a variety of compounds, including hydrophobic, hydrophilic, electron rich and electron deficient molecules. For the assay, an aqueous solution of the selected pollutant (0.1 mM, 3 mL) was quickly passed through porous polymers (3 mg) within 20 s. The removal efficiency was calculated based on the change of UV-Vis absorbance. As summarized in Table 1, P-PAP[n]s are efficient against most of the pollutants (>80% removal efficiency). The removal efficiency of P-PAP[5] is similar or better compared to activated carbon (AC, Norit® SA 2) and cyclodextrin based porous polymer P-CDP.[29] The adsorption efficiency of P-PAP[6] is slightly higher than P-PAP[5] for most of the pollutants. It is intriguing that P-PAP[n]s are highly effective against the electron deficient compound paraquat and heavy metal Cu^{2+}. P-PAP[5] is able to remove 88% of Cu^{2+} and almost the complete quantity of paraquat (97%). By comparison, activated carbon is barely effective against these two hydrophilic pollutants.

We studied the adsorption kinetics and isotherms, choosing paraquat as the model pollutant and P-PAP[5] as the adsorbent. The batch adsorption kinetics is shown in Fig. 3a. We observed a very rapid adsorption, reaching equilibrium almost instaneously (within 10 s). The experimental results were fitted to a pseudo-second-order kinetic model (Fig. 3b).[31] The apparent rate constant (k_2) of paraquat is 33.3 g·mg^{-1}·min^{-1}, which is 5 to 5.5×10^4 times faster than previously reported paraquat adsorbents (Table S1). This fast adsorption enables P-PAP[5] a promising adsorbent for flow-through paraquat treatment. We then carried out flow-through adsorption experiments. Paraquat (0.1 mM, 3 mL), P-PAP[5] (3 mg), and a filter with cross area of 1.33 cm^2 were used for each test. Three different flow rates, 14.7 mL min^{-1} (12 s), 9.0 mL min^{-1} (20 s), and 3.0 mL min^{-1} (60 s), were tested (Fig. 3c). P-PAP[5] was able to remove 97% of the paraquat from the solution even at the highest flow rate. By comparison, AC removed 13% of the pollutant at this rate, and its uptake efficiency only improved slightly as flow rates decreased.

The adsorption capacity (q_e, mg g^{-1}) was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)VM_w}{m}$$

Here V (L) is the volume of the paraquat solution. C_0 and C_e are the initial and final paraquat concentrations (mM). M_w (g mol^{-1}) is the molecular mass of paraquat. m is the mass of adsorbent (g).

The adsorption isotherms are depicted in Fig. 3d, which

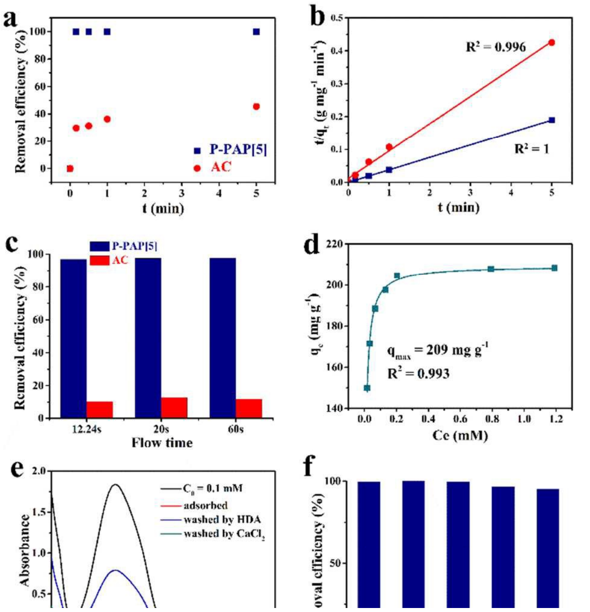


Fig. 3 (a) Time-dependent removal of paraquat by P-PAP[5] and AC in batch adsorption experiments. (b) Pseudo-second-order plots of batch adsorption kinetics. (c) Removal of paraquat in flow-through adsorption experiments with different flow rates. (d) Langmuir isotherm of paraquat adsorption by P-PAP[5]. (e) UV-vis spectra of the guest displacement assay. (f) Paraquat removal efficiency by P-PAP[5] after consecutive regeneration cycles.

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follows the Langmuir isotherm model.[32] The equation of Langmuir isotherm model was applied to fit the data:

$$q_e = \frac{q_{max} b C_e}{1 + bC_e}$$

Here $q_{\max}$ (mg g^{-1}) is the maximum adsorption capacity of pollutants, and b is the equilibrium constant. The maximum adsorption capacity $q_{\max}$ is calculated to be 209 mg/g. Its adsorption capacity is superior compared to most previously reported adsorbents for paraquat (Table S1).

To study the mechanism of adsorption, we carried out guest displacement assays (Fig. 3e). PA[n]s are known to be hosts for paraquat and linear guests, such as hexanediamine (HDA).[33] A solution of paraquat (0.1 mM, 3 mL) was passed through P-PAP[5] (3 mg). The paraquat loaded P-PAP[5] was then treated with a solution of HDA dihydrochloride salt (4 mM, 3 mL), which acts as a competing guest to displace paraquat from the cavity of PA[5]. In the control experiment, a solution of $CaCl_2$ with the same concentration and volume was used. UV-Vis absorbance showed that HDA replaced 43% of the absorbed paraquat, while $CaCl_2$ only replaced 7%. This assay indicates the adsorption of paraquat may be due to host-guest interactions. Next, we studied the mechanism on the molecular level. As shown in ^{1}H NMR spectra, in the presence of water soluble PA[5] or PA[6], the aromatic protons of paraquat have a significant upfield shift, which indicates the host-guest encapsulation inside the cavity (Fig. S9a-c). By contrast, when the building unit of water soluble PA[n]s is present, we do not observe any shift for paraquat resonances, demonstrating the host-guest interaction is due to the macrocyclic cavity (Fig. S9d). Ogoshi and Li have reported the encapsulation of paraquat inside the cavity of PA[n]s in solution phase.[18,34] The electron rich PA[n] cavity could complex electron deficient paraquat via charge-transfer and electrostatic interactions, which may play a vital role in the adsorption of cationic pollutants (paraquat and Cu^{2+}). On the other side, hydrophobicity and π-π interactions may be important for the adsorption of hydrophobic pollutants, such as BPA.

To study the feasibility P-PAPs as adsorbents, it was necessary to study the regeneration and reusability of these materials. Desorption experiments were performed by washing the materials (3 mg) with methanol (3 mL) at room temperature for 5 min. Five consecutive paraquat adsorption/desorption cycles were performed and the removal efficiency in each cycle is shown in Fig. 3f. The paraquat removal efficiency only decreased slightly (from 99% to 95%) after five regeneration cycles. With a low synthetic cost and reusability, P-PAP[n]s are economical and practical to be used for waste-water treatment.

In summary, we have developed new PA[n] based porous materials. We have demonstrated their ability to rapidly remove various micropollutants from water with a high efficiency. These materials are especially efficient to sequester electron-deficient pollutant paraquat via host-guest interactions. These PA[n] based materials are superior paraquat adsorbents, with low synthetic costs, a fast uptake kinetics, high removal capacity and regeneration ability. These porous materials are promising to have applications for flow-through waste-water treatment. Their potential applications also include molecular enrichment and chemical separation.

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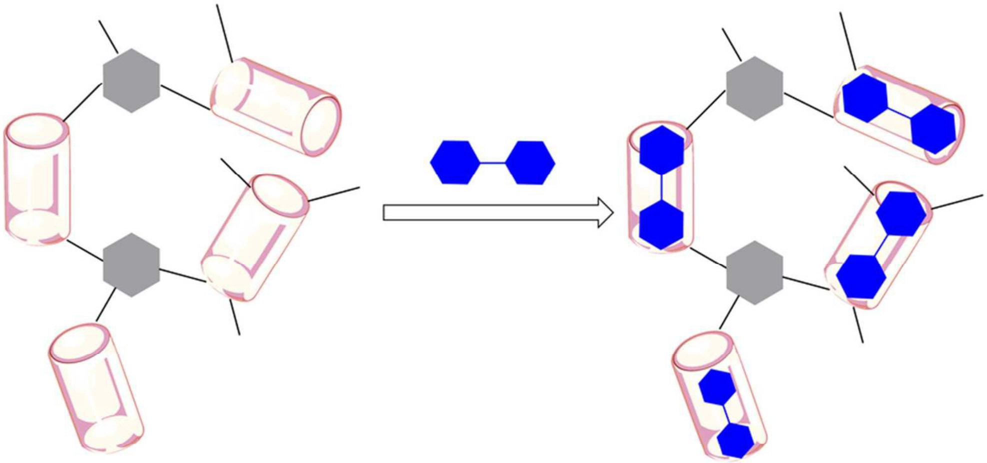

Pillararene based polymers are superior adsorbents for paraquat

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