# High-Efficiency Separation of Aromatic Sulfide from Liquid Hydrocarbon Fuel in Conjugated Porous Organic Framework with **Polycarbazole Unit**

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#### Supporting Information

**ABSTRACT:** We synthesized three conjugated polycarbazole porous organic frameworks named o-Cz-POF, m-Cz-POF, and p-Cz-POF for hydrocarbon fuels' adsorptive desulfurization. The carbazole building blocks possessed ortho, meta, and para steric configuration, which resulted in POFs exhibiting adjustable specific surface area and pore structure. Adsorption kinetics experiments and DFT calculations were carried out to understand the competitive adsorption of 3-methylthiophene and octane in the Cz-POF. The instantaneous adsorption rate and adsorption energy calculation analyses gave a convincing demonstration on preferential selective adsorption of 3methylthiophene in Cz-POFs. Furthermore, the fixed bed



breakthrough experiment demonstrated that the Cz-POFs can selectively adsorb 3-methylthiophene efficiently, and hydrocarbon fuel with sulfide content close to 0 ppm was obtained. The features of high stability and high desulfurization efficiency of Cz-POFs make them hold the promise as a new type of porous adsorbent for ultradeep adsorption desulfurization.

KEYWORDS: porous organic framework, desulfurization, polycarbazole, conjugated polymer, competitive adsorption

#### INTRODUCTION

Desulfurization of liquid hydrocarbon fuels has attracted wide attention due to the severe atmospheric pollution caused by sulfur-containing fuel consumption. $^{1-3}$  Governments have imposed more and more pressure on petroleum refineries to produce ultralow sulfur level fuel in view of environmental sustainability.<sup>4-7</sup> Catalytic hydro-desulfurization technology is for now the most mainstream technique for the industrialization of removing mercaptans and thioether, but it is unreliable for eliminating aromatic sulfur compounds.<sup>8-10</sup> Furthermore, catalytic hydro-desulfurization is conducted at high temperatures and pressures (>300 °C, hydrogen pressure of 20-100 atm), which require high energy consumption and come the side-effects of large octane loss.<sup>6,11</sup> One alternative technology, adsorptive desulfurization, has attracted enormous attention by virtue of its high efficiency, low consumption, and ultradeep desulfurization without changing the characteristics of gasoline.<sup>12</sup> More importantly, liquid fuels with an ultralow

sulfur content of less than 10 ppm can be achieved by adsorption desulfurization, which can meet the increasingly stringent vehicle exhaust regulations worldwide.<sup>13–15</sup>

Porous adsorbents with good chemical stability, high aromatic sulfide selectivity, large adsorption capacity, and superior reusability are highly desired for adsorptive desulfurization. Nanoporous materials, including zeolites,<sup>16,17</sup> activated carbon,<sup>18</sup> and metal organic frameworks (MOFs),<sup>17,19–22</sup> have been extensively exploited for selectively deep desulfurization in gasoline. Commercialized zeolite and activated carbon are good candidates for adsorptive desulfurization, but a trade-off between the high sulfide selectivity and the large adsorption capacity limits their further applications. In the past decade, MOFs as a desulfurization adsorbent have attracted increasing

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attention because of their large surface areas and controllable pore sizes. However, the physicochemical stability of MOFs against hash industrial conditions such as strong acid/alkali environments and high temperature is still questioned.

Porous organic frameworks (POFs) as a branch of emerging nanoporous materials have shown excellent potential in the field of gas storage, catalysis, and energy storage benefiting from their high specific surface area, tunable pore property, and excellent thermal and chemical stability.<sup>23–25</sup> Several types of porous organic frameworks have been developed in the past few years, and notable examples include covalent organic frameworks (COFs),<sup>26,27</sup> covalent triazine-based frameworks (CTFs),<sup>28-3</sup> <sup>2</sup> polymers of intrinsic microporosity (PIMs),<sup>33,34</sup> porous aromatic frameworks (PAFs),<sup>35,36</sup> conjugated microporous polymers (CMPs),<sup>37</sup> and hyper-cross-linked polymers (HCPs),<sup>38,39</sup> among others. Conjugated POFs are ideal candidates for aromatic sulfide separation because of their large conjugated aromatic skeletons, adjustable pore structure and size, and persistent porosity. First, the wide extensively conjugated aromatic skeletons in POFs increase aromatic sulfide adsorption selectivity by the high-density  $\pi - \pi$ interactions.<sup>14,25</sup> Second, the high pore volume and innerconnected pore structure of POFs minimize the diffusion resistance of adsorbates.<sup>40</sup> Third, the rigid frameworks and intrinsic persistent porosity of POFs are robust enough for use in harsh environments, which determines their sustainable reuse.41

Oxidatively coupling carbazole-POFs by FeCl<sub>3</sub> is a costeffective methodology for preparing conjugated POFs. The recently reported porous polycarbazole networks exhibit high CO2 uptake and photoreduction activity owing to their conjugated skeletons and abundant heteroatoms.<sup>24,25</sup> The extended  $\pi$ -conjugated polycarbazole units in the POFs render them promising applications in adsorptive desulfurization. Herein, we report three conjugated polycarbazole POFs with high surface areas (up to 2506  $m^2 \cdot g^{-1}$ ) and a hierarchical pore structure to separate aromatic sulfides in gasoline for the first time. The carbazole linker monomers possess ortho, meta, and para steric configuration, resulting in POFs exhibiting pore size distributions from a dominant microporous to micromesoporous hierarchical pore structure. The vapor adsorption experiments demonstrated that m-Cz-POF can adsorb 7.76 mmol/g of 3-methylthiophene under 25 °C and 2.58 kPa, which is much higher than the reported porous adsorbents. Adsorption kinetics test results showed that the Cz-POFs can adsorb aromatic sulfide at a much higher adsorption rate compared with simulative gasoline n-octane. The density functional theory (DFT) calculation indicated that Cz-POF had a higher binding energy with 3-methylthiophene than noctane, benefiting from their stronger conjugate interaction. Moreover, the fixed bed breakthrough experiment demonstrated that the m-Cz-POF can selectively adsorb 3methylthiophene efficiently; thus, the pure n-octane can be obtained via one adsorption process.

#### 1. EXPERIMENTAL SECTION

**1.1.** Synthesis. Synthesis of 4-Bromo-2,6-di(9H-carbazol-9yl)benzonitrile (1a). 9H-Carbazole (5.01 g, 30 mmol) was dissolved in 50 mL of anhydrous DMF (N,N-dimethylformamide), and the solution was added dropwise into a mixture of t-BuOK (4.49 g, 40 mmol) and 50 mL of anhydrous DMF within 20 min. After the system was stirring for 3 h at room temperature, 15 mL of anhydrous DMF solution containing 4-bromo-2,6-difluorobenzonitrile (3.27 g, 15 mmol) was injected into it within 20 min. The solution was stirred at 90 °C for 12 h and then cooled down. The resulting solution was poured into ice water. The white powder solid was filtered and dried in vacuum overnight, and then, it was further purified by column chromatography, resulting in a white solid (4.98 g). Yield: 74%. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$ /ppm: 8.44 (s, 1H), 8.32 (dt, *J* = 7.7, 1.0 Hz, 2H), 7.61–7.53 (m, 4H), 7.41 (ddd, *J* = 8.0, 6.5, 1.7 Hz, 2H).

Synthesis of 3,3",5,5"-Tetra(9H-carbazol-9-yl)-[1,1':2',1"-terphenyl]-4,4"-dicarbonitrile (**2a**). The Suzuki reaction proceeded under nitrogen protection. 4-Bromo-2,6-di(9H-carbazol-9-yl)-benzonitrile) (1.0 g, 1.96 mmol), 1,2-phenylenediboronic acid bis(pinacol) ester (0.16 g, 0.98 mmol), palladium tetrakis(triphenylphosphine) (0.06 g, 0.05 mmol), and potassium carbonate (0.54 g, 3.92 mmol) in a mixture of tetrahydrofuran (16 mL) and H<sub>2</sub>O (8 mL) was refluxed for 48 h. Water (25 mL) was added to quench the reaction, and the mixture was then extracted with dichloromethane. The organic solution was washed with water and dried over anhydrous sodium sulfate. The crude product was purified by using column chromatography with dichloromethane as the eluent to give a yellow solid (0.67 g). Yield: 73%. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.29–8.24 (m, 8H), 8.15 (s, 4H), 7.76 (dt, J = 7.5, 3.7 Hz, 2H), 7.62 (dq, J = 6.9, 3.9 Hz, 2H), 7.30–7.18 (m, 24H).

Synthesis of 3,3'',5,5''-Tetra(9H-carbazol-9-yl)-[1,1':3',1''-terphenyl]-4,4''-dicarbonitrile (**2b**). A procedure similar to that used for compound **2a** was followed but with 1,3-phenylenediboronic acid bis(pinacol) ester (0.16 g, 0.98 mmol) instead of 1,2-phenylenediboronic acid bis(pinacol) ester, yielding the product as a light yellow solid (0.75 g). Yield: 81%. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$ 8.56 (s, 4H), 8.41 (d, J = 1.9 Hz, 1H), 8.26 (d, J = 7.7 Hz, 8H), 8.08 (dd, J = 7.9, 1.8 Hz, 2H), 7.65 (t, J = 7.9 Hz, 1H), 7.54–7.44 (m, 16H), 7.37–7.30 (m, 8H).

Synthesis of 3,3",5,5"-Tetra(9H-carbazol-9-yl)-[1,1':4',1"-terphenyl]-4,4"-dicarbonitrile (**2c**). A procedure similar to that used for compound **2a** was followed but with 1,4-phenylenediboronic acid bis(pinacol) ester (0.16 g, 0.98 mmol) instead of 1,2-phenylenediboronic acid bis(pinacol) ester, yielding the product as a yellow solid (0.83 g). Yield: 80%. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.51 (s, 1H), 8.29 (d, *J* = 7.7 Hz, 2H), 8.14 (s, 1H), 7.59–7.48 (m, 4H), 7.36 (t, *J* = 7.3 Hz, 2H).

Synthesis of o-Cz-POF ( $P_1$ ). The synthesis of o-Cz-POF was prepared using a reported procedure by Han et al.<sup>23</sup> Compound **2a** (0.1 g, 0.106 mmol) was dissolved in anhydrous chloroform (50 mL) under argon protection. The monomer solution was added dropwise to dry chloroform solution (20 mL) of anhydrous ferric chloride (250 mg, 1.5 mmol). The resulting mixture was stirred at room temperature for 72 h. Methanol (60 mL) was added to quench the reaction and then continuously stirred for another hour. After filtration, the obtained polymer was then washed in concentrated hydrochloric acid for 2 h and in water and THF for 0.5 h, individually. The obtained product was then purified with THF for another day using Soxhelet extraction and dried overnight in vacuum at 120 °C. Yield: 96 mg (96%). Found element analysis calcd (%) for C<sub>68</sub>H<sub>32</sub>N<sub>6</sub>: C, 70.5; H, 3.16; N, 8.03. Theoretical: C, 87.6; H, 3.4; N, 9.0.

Synthesis of m-Cz-POF ( $P_2$ ). The porous material was obtained following the same procedure described above for o-Cz-POF with **2b** (0.06g, 0.064 mmol). Yield: 91 mg (91%). Found element analysis calcd (%) for C<sub>68</sub>H<sub>32</sub>N<sub>6</sub>: C, 72.42; H, 3.08; N, 8.2. Theoretical: C, 87.6; H, 3.4; N, 9.0.

Synthesis of p-Cz-POF ( $P_3$ ). The porous material was obtained following the same procedure described above for o-Cz-POF with 2c (0.08g, 0.085 mmol). Yield: 87 mg (87%). Found element analysis calcd (%) for C<sub>68</sub>H<sub>32</sub>N<sub>6</sub>: C, 69.38; H, 2.789; N, 8.16. Theoretical: C, 87.6; H, 3.4; N, 9.0.

#### 2. RESULTS AND DISCUSSION

**2.1. Syntheses and Characterization of o-Cz-POF,** *m*-**Cz-POF, and** *p*-**Cz-POF.** In order to achieve the desired desulfurization efficiency, POFs with high specific surface area and a suitable pore structure are the main characteristics we pursued, so the monomers with ortho, meta, and para steric

Scheme 1. Synthetic Method for o-Cz-POF, m-Cz-POF, and p-Cz-POF



configuration (monomers 2a-c) were exploited by the Suzuki coupling reaction (Scheme 1). In the subsequent polymerization, we chose oxidative coupling promoted by FeCl<sub>3</sub> as the given polymerization, which has been proven as an effective, low-cost, and facile way to prepare porous organic materials.

The obtained o-Cz-POF, m-Cz-POF, and p-Cz-POF powders are insoluble in common solvents such as methyl alcohol, tetrahydrofuran, dioxane, DMF, and DMSO, showing that the powders are highly polymerized networks. In particular, all three polymers show excellent chemical stability even under the strong acid condition, since the compounds were stirred in concentrated hydrochloric acid to remove FeCl<sub>2</sub>. FT-IR spectra also demonstrated the coupling polymerization of carbazole monomers. The observed peak at ~721 cm<sup>-1</sup> assigned to the bisubstituted phenyl ring in the carbazole monomer is decreased, and the peak at  $\sim 800$  cm<sup>-1</sup>, which was attributed to the trisubstituted phenyl ring in carbazole, is well observed (Supporting Information, Figure S1 and Figure 1a for o-Cz-POF).<sup>42-44</sup> Thermal gravimetric analysis of three POFs illustrated that they all have remarkable thermal stability, and the decompositions temperatures of o-Cz-POF, m-Cz-POF, and *p*-Cz-POF are 473, 471, and 478 °C, respectively (Figures 1b and S2-4). The broad and noncharacteristic peaks of PXRD analysis indicated that all the synthesized POFs are at an amorphous state (Figure S5). The solid-state CP/MAS  $^{13}$ C NMR spectrum for the *o*-Cz-POF is shown in Figure 1c (Figure S6 for the other two polymers). The single peak at 141.3 ppm is ascribed to the substituted carbons of phenyl connecting with the nitrogen atom. The especially high peak at 125.5 ppm is assigned to other benzene substituted carbon atoms and also to the C atom in the cyanide group.<sup>25</sup> The unsubstituted phenyl carbons located at 110 ppm are shown as a single peak.<sup>45</sup> Scanning electron microscope (SEM) images revealed that the morphology of the Cz-POFs is aggregated irregular spherical particles with diameters of 200–1000 nm (Figure 1d-f), which is completely different from the morphology of the monomers (Figure S7).

**2.2. Porosity Measurements.** The porous properties of *o*-Cz-POF, *m*-Cz-POF, and *p*-Cz-POF were provided by N<sub>2</sub> adsorption/desorption measurements at 77 K. As shown in Figure 2a–c, all three of the adsorption isotherms show typical microporous properties at relatively low pressures ( $P/P_0 < 0.05$ ), while the gradual increase under high pressures ( $P/P_0 = 0.05-0.9$ ) was due to the existence of mesopores in the polymers. Furthermore, the coexistence of both the micropores and mesopores results in a hysteresis between the adsorption



Figure 1. (a) FT-IR spectra of monomer o-Czph and o-Cz-POF; (b) TGA of Cz-POFs; (c) solid-state CP-MAS <sup>13</sup>C NMR spectrum of o-Cz-POF; SEM images of o-Cz-POF (d), m-Cz-POF (e), and p-Cz-POF (f).

and desorption curves observed in all three polymers, confirming the hierarchical micromesoporous network structure of the synthesized POFs. The o-Cz-POF shows BET surface areas of 1337  $m^2 g^{-1}$ , while the Langmuir surface areas are increased to 1769 and 1666 m<sup>2</sup>·g<sup>-1</sup> for *m*-Cz-POF and *p*-Cz-POF, respectively (Figures S8–S10). The pore size distributions (PSDs) of the three Cz-POFs are calculated according to nonlocal density functional theory (NLDFT), and the results are shown in Figure 2d-f. The PSDs of o-Cz-POF are predominantly in the microporous range, mainly centered at 0.54 nm. Meanwhile, for m-Cz-POF and p-Cz-POF, the micropores are centered at 0.58 and 0.56 nm, respectively, and the m-Cz-POF and p-Cz-POF show an increase of the mesopore portion in both the PSD and pore volume. These results suggested that the change of the carbazole and benzene connection configuration in building blocks can regulate the surface areas, PSDs, and pore volumes of resulting POFs. The other porous properties of the samples such as the BET and Langmuir surface areas, pore size, and microporous and total porous volume are listed in Table 1.

**2.3. Vapor Adsorption of 3-Methylthiophene and** *n*-**Octane.** Giving credit to the considerable high surface areas and porosity of *o*-Cz-POF, *m*-Cz-POF, and *p*-Cz-POF, we concentrated on assessing their capability in adsorption desulfurization. The main harmful substance in gasoline is thiophene compounds, among which alkyl substituted thiophene compounds account for a large portion. Herein, we measured the vapor adsorption performance of Cz-POFs for 3-methylthiophene and *n*-octane at 298 K, separately. As shown in Figure 3, the uptake of 3-methylthiophene in the Cz-POFs is increased gradually as the pressure increases (Figure 3a). The highest uptake amount of 3-methylthiophene is

observed in m-Cz-POF, which could reach 7.762 mmol/g (248.4 mg of S/g) at 298 K. This value is far beyond those of the porous absorbents previously reported (Figure 4).<sup>13-15,18,20,22,46-53</sup> As for o-Cz-POF and p-Cz-POF, the maximum 3-methylthiophene absorption amounts are 6.266 and 7.599 mmol/g (200.5 and 243.2 mg of S/g), respectively, which indicated that the aromatic sulfide adsorption capacity was positively correlated with their surface area. The uptake of n-octane for o-Cz-POF, m-Cz-POF, and p-Cz-POF was 5.006, 6.238, and 5.903 mmol/g, respectively (Figure 3b). As shown in Figure 3, the adsorption capacity of *n*-octane was much lower than that of 3-methylthiophene under all partial pressures. The apparent differences in adsorption capacity between 3-methylthiophene and *n*-octane enabled us to further study its adsorption desulfurization performance. It is worth to mention that all three POFs exhibited impressive recyclability and still held an unchanged adsorption capability of 3methylthiophene after testing was repeated several times.

**2.4.** Adsorption Kinetics of 3-Methylthiophene and *n*-Octane. In the adsorption desulfurization process, the adsorption capacity in equilibrium and the adsorption kinetics parameters are the basis for selecting suitable adsorbents, designing the adsorption process, and analyzing the economy of the adsorption system. In the actual separation process, the contact time between adsorbents and sulfides is variable. Therefore, it is quite essential to study the time-variation adsorption kinetics of Cz-POFs for 3-methylthiophene and *n*-octane were investigated by utilizing a gravimetry vapor sorption analyzer under the same partial pressure (0.25  $P_0$ ). The instantaneous adsorption rate curves of *m*-Cz-POF for 3-methylthiophene and *n*-octane are shown in Figure 5a,b. The



Figure 2. (a-c) Nitrogen adsorption and desorption isotherms and the NLDFT pore size distributions of *o*-Cz-POF (d), *m*-Cz-POF (e), and *p*-Cz-POF (f).

Table	1.	Porosity	Parameters	for o-	, m-	, and	p-Cz-POFs
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polymers	SA <sub>BET</sub> <sup>a</sup>	SA <sub>LANG</sub> <sup>a</sup>	$V_{\rm micro}^{\ \ b}$	$V_{\rm total}{}^{c}$	$V_{ m micro}/V_{ m total}$
o-Cz-POF	1337	1825	0.54	0.86	0.63
m-Cz-POF	1769	2506	0.67	1.09	0.61
p-Cz-POF	1666	2198	0.59	1.04	0.57

<sup>*a*</sup>Surface areas (m<sup>2</sup>·g<sup>-1</sup>) were calculated from the nitrogen adsorption branch based on the BET model and Langmuir model, respectively. <sup>*b*</sup>Micropore (diameters < 2 nm) volume was calculated at 77 K using the N<sub>2</sub> NLDFT model. <sup>*c*</sup>Total pore volume (cm<sup>3</sup> g<sup>-1</sup>) was calculated at  $P/P_0 = 0.99$ .

m-Cz-POF exhibited the maximum absorption rate at the beginning for both vapors, and then, the adsorption rate decreased gradually along with the increase of time. The maximum adsorption rate of 3-methylthiophene on m-Cz-POF

was as high as 1.65 mmol/(g·min), while that is 1.01 mmol/(g·min) for *n*-octane. Moreover, the adsorption rate of 3-methylthiophene was much faster than that of octane during the whole test range, which means 3-methylthiophene is preferential for adsorption in the *m*-Cz-POF. Because of the huge adsorption velocity difference between thiophene and *n*-octane, it can be concluded that 3-methylthiophene will be preferentially adsorbed in the POFs and occupy the pores, thereby resulting in efficient desulfurization in hydrocarbon fuel.

To further understand the adsorption differences between 3methlythiophene and *n*-octane, we performed theoretical molecular adsorption simulations on Cz-POFs. Based on the linear combination of atomic orbitals (LCAO), DFT calculations were performed using the DMol<sup>3</sup> package of



Figure 3. Adsorption isotherms of 3-methylthiophene (a) and n-octane (b) for o-Cz-POF, m-Cz-POF, and p-Cz-POF, at 298 K.



Figure 4. (a) Comparison of desulfurization S uptake  $(q_m)$  versus specific surface area of multiple adsorbents  $(S_{BET})$  and (b) comparison of S uptake  $(q_m)$  with former works.



Figure 5. (a) Instant adsorption rate of 3-methylthiophene uptake at 298 K; (b) instant adsorption rate of n-octane uptake at 298 K.

(1)

Material Studio.<sup>10</sup> The molecular adsorption of 3-methlythiophene and n-octane on the polymers surface is expressed by follow equation

The molecular and dissociative adsorption energy ( $\Delta E_{ads}$ ) were calculated by the DFT calculation results using the follow equations, respectively

surface + A (adsorption)  $\Leftrightarrow$  A - surface

$$\Delta E_{\rm ads} = E_{A-\rm surface} - E_{\rm clean \ surface} - E_A \tag{2}$$

$$\Delta E_{\rm ads} = E_{\rm adsorption \ system} - E_{m - Cz - POF} - E_{\rm adsorbate} - BSSE$$
(3)

In eq 3,  $E_{m-Cz-POF}$ ,  $E_{adsorbate}$ ,  $E_{adsorpation system}$ , and BSSE are the total electronic energy of the synthesized polymer, the free 3-methlythiophene or *n*-octane, the adsorbed surface, and the basis set superposition error, respectively.

As shown in Figure S11a,b, the  $\Delta E_{ads}$  values of 3methlythiophene on the two carbazole rings in the selected *m*-Cz-POF segments were calculated as -0.82 and -0.84 eV, respectively, and that on the benzene rings was enhanced to -0.91 eV (Figure 6d). The layer distance between thiophene



Figure 6. Simulated molecular model of adsorbates (a) 3methylthiophene and (b) the basic fragment of m-Cz-POF and (c) n-octane given by Material Studio. Optimized adsorption locating sites of 3-methylthiophene (d) and n-octane (e) on m-Cz-POF.

plane and benzene was 3.504 Å, which was close to the distance between the  $\pi-\pi$  stacking layers of graphite. The negative values indicated that the adsorption process is exothermic. The large of the  $\Delta E_{ads}$  absolute value indicated the strength of the interaction energy between the adsorbent and the adsorbate. Approximate  $\Delta E_{ads}$  values in all three adsorption sites revealed that there may be a synergistic effect in the 3-methlythiophene uptake for Cz-POFs. The same

optimization approach was applied to the comparative adsorbate, n-octane, and the final structure is shown in Figure 6e. When the *n*-octane was selectively adsorbed on benzene rings, the long chain was located along the conjugated benzene skeleton with a  $\Delta E_{ads}$  of -0.47 eV. (Supporting Information, Figure S11) As for locating above carbazole rings, the  $\Delta E_{ads}$ was enhanced to -0.52 eV, and the distance is 3.513 Å to the carbazole ring. The optimal adsorption energy of 3methlythiophene (-0.91 eV) in Cz-POF fragments was approximately 43% higher than that of *n*-octane (-0.52 eV), which suggested that Cz-POFs had a stronger interaction with 3-methlythiophene than n-octane. The introduction of the conjugated aromatic skeleton into the Cz-POFs would clearly enhance the aromatic sulfide adsorption. Both adsorption kinetics and adsorption energy simulation results highlighted that Cz-POFs would promise a better adsorption desulphurization performance.

2.5. Fixed Bed Breakthrough Experiment. To further explore the adsorption desulphurization ability of Cz-POFs in practical separation processes, we designed a breakthrough experiment to evaluate their performance under kinetic dynamic conditions.<sup>54</sup> The breakthrough tests of a mixture solution (650 ppm of 3-methlythiophene in n-octane, simulated sulfur content in gasoline) were performed by using a fixed bed column packed with Cz-POFs under a pressure of 0.22 MPa.<sup>55</sup> The mixed solution gradually permeated and passed through the fixed bed, and the filtrate was subjected to analysis in a gas chromatograph at intervals (Figure S12). The breakthrough curves of *m*-Cz-POF and *o*-Cz-POF are shown in Figure 7. As expected from results of the adsorption kinetics and adsorption energy analyses, in each case, *n*-octane penetrated through the bed first, whereas the 3methlythiophene was retained in the POF column. Within 26 min, the m-Cz-POF adsorbed 3-methlythiophene, and the outlet liquid contained pure n-octane with a sulfide content close to 0 ppm (Figure 7b). After 38 min, the 3methlythiophene concentration of the outlet liquid reached the feed composition, indicating the saturation of the POF adsorption column. As for o-Cz-POF with the smallest BET surface areas, 3-methlythiophene broke through the column around 9 min, and the column reached adsorption saturation in 20 min (Figure 7a), which means Cz-POFs with large surface areas have a better adsorption capacity in desulphurization. Under dynamic breakthrough conditions, the adsorption



Figure 7. Effluent concentration of o-Cz-POF (a) and m-Cz-POF (b) at different times, in fixed bed experiments.

of molecules on the adsorbent was a competitive procedure. The 3-methlythiophene with strong adsorption energy was preferentially adsorbed in Cz-POFs. After adsorption of 3-methlythiophene into the POF channel, only a small amount of pore volume was left for *n*-octane (Figure S13). Thus, the adsorption of *n*-octane in the Cz-POF was suppressed, and it passed through the packing column fluently. We also study the recyclability of the POF adsorbent used in the breakthrough experiments. As shown in Figure S14, the Cz-POF can be easily rinsed and regenerated by washing it with MeOH or heating at 120 °C under vacuum. The adsorption efficiency of the recycled Cz-POF retains 98% of the original capacity after six cycles.

#### 3. CONCLUSIONS

In summary, three new carbazole porous organic frameworks named o-Cz-POF, m-Cz-POF, and p-Cz-POF had been successfully synthesized via facile FeCl<sub>3</sub> promoting oxidative polymerization. The specific surface area and microporous pore volume of POF can be adjusted by the ortho, meta, and para steric configuration of the carbazole monomers. The m-Cz-POF showed the highest surface area of 2506  $m^2 \cdot g^{-1}$  and pore volume of 1.09 cm<sup>3</sup>·g<sup>-1</sup>, respectively. The conjugated polycarbazole POFs were used to separate aromatic sulfides in gasoline. The m-Cz-POF can adsorb 7.76 mmol/g of 3methylthiophene (248.32 mg of S/g) under 25 °C and 2.58 kPa, which was much larger than that of the reported porous adsorbents. Adsorption kinetics experiments showed that the adsorption rate of 3-methylthiophene on m-Cz-POF is 1.65 mmol/(g·min), which is much higher than that of *n*-octane (1.01 mmol/(g·min)). Adsorption kinetics experiments and adsorption energy DFT calculations were performed to understand the competitive adsorption between 3-methylthiophene and octane in the Cz-POF. The instant adsorption rate and adsorption energy analyses gave a convincing demonstration on the preferential selective adsorption of 3methylthiophene in Cz-POFs. Moreover, the dynamic breakthrough tests proved the Cz-POFs can separate 3-methlythiophene in an n-octane mixture based on their different adsorption energies in an actual adsorption desulphurization process. For the first time, we systematically investigated Cz-POFs for the adsorption desulphurization under both equilibrium and kinetic conditions. The combination of the synthetic feasibility, physicochemical stability, and high desulfurization efficiency commented on above make Cz-POFs as promising candidates for liquid hydrocarbon fuels' desulfurization adsorbents and other separation applications.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b15815.

Materials and testing method; FT-IR curves of solid monomers and polymers; thermal gravimetric analysis curves of solid samples; powder X-ray diffraction of powder polymers; solid-state CP/MAS <sup>13</sup>C NMR spectrum of both monomers and polymers; <sup>1</sup>H NMR spectrum of each unit; BET plots of three polymers; DFT calculation on different adsorption sites of both adsorbates (PDF)

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#### Notes

The authors declare no competing financial interest.

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