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Fabrication of Isoreticular Metal−Organic Framework Coated Capillary Columns for High-Resolution Gas Chromatographic Separation of Persistent Organic Pollutants

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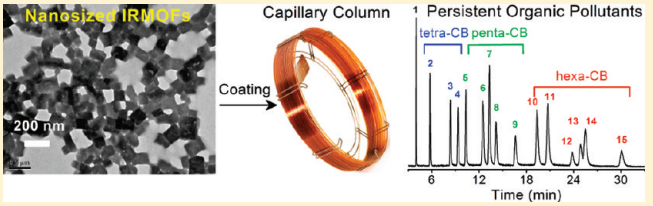
Supporting Information

ABSTRACT: The unusual properties of metal−organic frameworks (MOFs), such as permanent nanoscale porosity, high surface area, uniformly structured cavities, and the availability of in-pore functionality and outer-surface modification, are advantageous for diverse applications. However, most existing methods for the synthesis of nanosized MOFs require an activation procedure or auxiliary stabilizing agents. Here we report a 1-min, room-temperature approach for the synthesis of nanosized isoreticular MOFs (IRMOFs) to fabricate IRMOF coated capillary columns for the high-resolution gas chromatographic separation of persistent organic pollutants (POPs), including polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), polybrominated diphenylethers (PBDEs), and hexachlorocyclohexanes (HCHs). The developed method allows the synthesis of well-shaped nanosized IRMOFs within 1 min at room temperature without the need for any activation procedure or auxiliary stabilizing agents. The IRMOF coated capillary columns offer good separation efficiency that is generally comparable to that of a commercial HP-5MS column for POPs. The IRMOF-1 and IRMOF-3 coated capillary columns gave the theoretical plate values of 2293 and 2063 plates m^{-1} for naphthalene, respectively, which are slightly smaller than those with a HP-5MS column (2845 plates m^{-1}). The IRMOF-1 coated capillary column offered good resolution for the separation of several intractable PAH isomer pairs, such as anthracene/phenanthrene, benzo[*a*]anthracene/chrysene, and benzo[*b*]fluoranthene/benzo[*k*]fluoranthene, with resolutions of 3.0, 1.1, and 4.1, respectively, which were difficult to be baseline separated on a HP-5MS column with a resolution of 1.0. In addition, the IRMOF-1 and IRMOF-3 coated capillary columns offered a clear group separation of the PCB isomers and a linear range covering three orders of magnitude. The relative standard deviations for the five replicate separations of PAHs were 0.23−0.26% and 2.1−4.5% for retention time and peak area, respectively. The fabricated IRMOF coated capillary columns have been shown to be very promising for the separation of POPs with good reproducibility, high resolution, great selectivity, and a wide linear range.



Metal−organic frameworks (MOFs) have received great attention because of their fascinating structures and intriguing applications in hydrogen storage, gas separation, catalysis, sensing, and imaging.[1−4] While most researchers have focused on the synthesis of MOFs with new and exotic topologies and porous networks, increasing efforts have been made to explore their potential for real applications. In the past decade, vapor-phase adsorption and the separation of small molecules, from hydrogen to xylene isomers, on MOFs have been extensively studied.[5] However, much less attention has been paid to the separation of larger molecules on MOFs, although several attempts have been made to use MOFs for the liquid-phase adsorption and separation of several drugs, dyes, pollutants, peptides, and proteins.[6−12] MOF packed columns have been successfully employed to separate molecules such as hydrocarbon isomers under high temperatures,[13−17] but larger molecules are hard to separate on MOF packed columns because of the poor resolution resulting from considerable diffusion resistance on bulky packing. These defects can be overcome by using MOF coated capillary columns because of the minimized diffusion resistance and the improved separation efficiency on thin coatings.[18,19]

Isoreticular MOFs (IRMOFs) are a group of cubic networks in which four Zn atoms bond to a single O atom, forming regular Zn_4O tetranuclear clusters that are connected by rigid dicarboxylate linkers to form Zn_4O(dicarboxylate)$_3$, giving high thermal stability, porosity, and a large accessible pore window (11.2 and 9.6 Å for IRMOF-1 and IRMOF-3, respectively) (Figure 1).[20] However, conventionally synthesized bulk IRMOFs are typically in the submillimeter scale, resulting in difficulties for coating capillary columns. Nanosized MOFs are the materials of choice for real applications.[21,22] Although a few direct mixing approaches have been reported for the preparation of MOFs in a reaction time scale from 5 min to 4 h,[23−26] most methods for the

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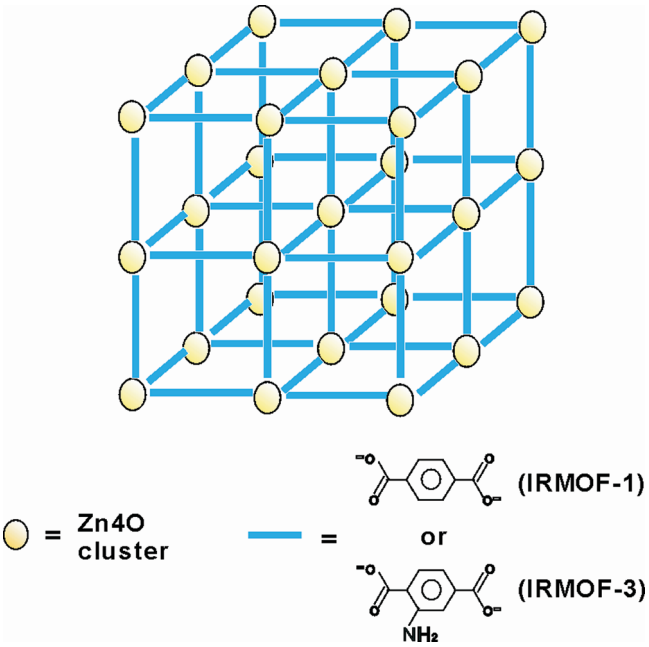

Figure 1. Schematic structure of IRMOF-1 and IRMOF-3.[20]

synthesis of nanosized MOFs require an activation procedure or auxiliary stabilizing agents, such as a microwave-[27,28] or ultrasonic-assisted strategy,[29] coordination modulation,[30,31] microemulsion,[21,32,33] or a self-assembled monolayer-stabilized strategy.[34−36]

Here we report a facile, rapid, and robust approach for the room-temperature synthesis of nanosized IRMOFs with great thermal stability and porosity for fabricating IRMOF coated capillary columns. The developed method allows the synthesis of well-shaped nanosized IRMOFs at room temperature within 1 min without the need for any activation procedure or auxiliary stabilizing agents. We use polychlorinated biphenyls (PCBs), polybrominated diphenylethers (PBDEs), polyaromatic hydrocarbons (PAHs), and hexachlorocyclohexanes (HCHs) as the targets because they are important groups of persistent organic pollutants (POPs), and they have significant adverse impacts on human health and the environment because of their toxicity, persistency, and bioaccumulation.[37,38] The effective separation of POPs, especially the isomer group, is challenging because of their high boiling points and similar chemical and physical properties. In this work, we show the great potential of the fabricated IRMOF coated capillary columns for the separation of POPs with good reproducibility, high resolution, great selectivity, and wide linear range.

EXPERIMENTAL SECTION

Chemicals and Materials. All of the chemicals used are at least analytical grade. Ultrapure water (18.2 MΩ cm) obtained from a Water Pro water purification system (Labconco Corporation, Kansas City, MO) was used throughout this work. *N,N*-Dimethylformamide (DMF) (Tianjin Standard Chemical Reagent Co. Ltd., Tiangin, China), $Zn(OAc)_2 \cdot 2H_2O$ (Aladdin Reagent Co. Ltd., Shanghai, China), terephthalic acid (Aladdin Reagent Co. Ltd., Shanghai, China), and 2-aminoterephthalic acid (Alfa Aesar, Ward Hill, MA) were used for the preparation of nanosized IRMOFs. CH_2Cl_2, NaOH, and HCl were obtained from Guangfu Fine Chemical Co. Ltd. (Tianjin, China). Fifteen standards of PCB congeners in an isooctane solution (2 mg L^{-1} for each) were obtained from the Institute of Agro-Environmental Protection (Tianjin, China). The congener structures can be obtained in the Supporting Information. The four PBDE standards (BDE-47, BDE-99, BDE-154, and BDE-153) in isooctane solution (50 mg L^{-1} for each) were purchased from AccuStandard (New Haven, CT). Acenaphthene (96%), fluorene (97%), phenanthrene (98%), fluoranthene (98%), and pyrene (98%) were purchased from Tianchang Chemical Co., Ltd. (Anshan, China). Naphthalene (99%), anthracene (99%), benzo[*a*]anthracene (99%), chrysene (99%), benzo[*b*]fluoranthene (99%), and benzo[*k*]fluoranthene (99%) were purchased from AccuStandard (New Haven, CT). Stock solutions of 50 mg L^{-1} for each PAH were prepared using isooctane as the solvent. α-HCH (99%), *β*-HCH (99%), *γ*-HCH (99%), and *δ*-HCH (98%) were purchased from Chengdu Chemical Factory (Chengdu, China). Stock solutions of 50 mg L^{-1} for α-HCH, *β*-HCH, *γ*-HCH, and *δ*-HCH were prepared using isooctane as the solvent. All standards and stock solutions were stored in the dark at 4 °C. Note: because of their high toxicity, great care should be taken to avoid direct contact with all of the POPs studied, and all of the solutions should be prepared in a well-ventilated hood.

Room-Temperature Synthesis of Nanosized IRMOFs. For a typical preparation of nanosized IRMOF-1, a 10 mL DMF solution of $Zn(OAc)_2 \cdot 2H_2O$ (80 mM) was rapidly poured into a 15 mL DMF solution of terephthalic acid (20 mM) at room temperature (20 °C). The mixture turned turbid immediately, and after 1 min, the nanocrystals were isolated by centrifugation (12000 rpm), washed with DMF and CH_2Cl_2, and redispersed in CH_2Cl_2 for coating capillary columns.

Similarly, IRMOF-3 was synthesized by rapidly pouring a 10 mL DMF solution of $Zn(OAc)_2 \cdot 2H_2O$ (80 mM) into a 15 mL DMF solution of 2-aminoterephthalic acid (20 mM) at room temperature (20 °C). The mixture turned turbid immediately, and after 1 min, the nanocrystals were isolated by centrifugation (12000 rpm), washed with DMF and CH_2Cl_2, and redispersed in CH_2Cl_2 for coating capillary columns.

Capillary Pretreatment and Preparation of IRMOF Coated Capillary Columns. A fused silica capillary (25 m long × 0.25 mm i.d., Yongnian Optic Fiber Plant, Hebei, China) was treated according to the following recipe before dynamic coating with the IRMOFs: the capillary was washed sequentially with 1 M NaOH for 2 h, ultrapure water for 30 min, 0.1 M HCl for 2 h, and ultrapure water until the outflow reached pH 7.0. The capillary was dried with a nitrogen purge at 120 °C overnight.

The IRMOF-1 and IRMOF-3 were coated onto the pretreated capillary columns by the following dynamic coating method:[18,19] a 0.2-mL CH_2Cl_2 suspension of IRMOF-1 or IRMOF-3 (0.5 mg mL^{-1}) was first filled into the capillary column (25 m long × 0.25 mm i.d.) under gas pressure, giving about a 4-m long plug in the capillary, and then it was pushed through the column at a velocity of 40 cm min^{-1} to leave a wet coating layer on the inner wall of the capillary column. The thickness of coating layer was controlled by the slurry concentration of IRMOFs and the velocity of the slurry plug for dynamic coating. To avoid the acceleration of the solution plug near the end of the column, a 1 m long buffer tube (0.25 mm i.d.) was attached to the capillary column end as a restrictor. After coating, the capillary column settled for 2 h for conditioning under nitrogen. An additional 6 h of further conditioning of the capillary column was needed using a temperature program including three steps: 25 °C for 10 min,

ramp from 25 to 300 °C at a rate of 1 °C min^{-1}, and 300 °C for 60 min.

Characterization of Nanosized IRMOFs. X-ray diffraction (XRD), thermal gravimetric analysis (TGA), and N_2 adsorption were employed to characterize the evacuated IRMOFs. Further purification of the nanosized IRMOFs was performed by washing with DMF three times, centrifuging at 12000 rpm for 5 min, and then washing with CH_2Cl_2 three times. The white solid obtained was evacuated under a vacuum at 150 °C for 12 h. The XRD patterns were recorded with a D/max-2500 diffractometer (Rigaku, Japan) using Cu Kα radiation (λ = 1.5418 Å). The TGA experiments were performed on a PTC-10A thermal gravimetric analyzer (Rigaku, Japan) from room temperature to 600 °C at a ramp rate of 10 °C min^{-1}. The BET surface area was measured on an ASAP 2010 micropore physisorption analyzer (Micromeritics, Norcross, GA) using nitrogen adsorption at 77 K in the range $0.02 \leq P/P_0 \leq 0.20$, respectively.

The size and morphology of the prepared IRMOFs were characterized by transmission electron microscopy (TEM). The TEM micrographs were recorded on a JEOL 100CX II microscope (Akishima, Japan) operating at a 100 kV accelerating voltage. To prepare the sample for TEM analysis, the copper grid (100 mesh) was immersed in the reaction mixture to directly load the resultant nanosized IRMOFs. After the quick removal of the residual mother liquid with a Kimwipe, the IRMOF loaded copper grid was put into the chamber of the transmission electron microscope as quickly as possible for TEM study.

The IRMOF coated capillary columns were characterized by scanning electron microscopy (SEM). The capillaries were cut to expose the inner wall for SEM measurement. For comparison, purified IRMOF-1 and IRMOF-3 in CH_2Cl_2 suspensions were loaded on two slides of glass and characterized by SEM, also. After the small amount of CH_2Cl_2 quickly vaporized, the slides were immediately put into the chamber of the scanning electron microscope. The SEM images were recorded on a Shimadzu SS-550 scanning electron microscope (Kyoto, Japan) at 15.0 kV.

Measurements via Gas Chromatography−Mass Spectrometry (GC-MS). All of the separations were performed on an Agilent 7890A/5975C GC-MS system (Agilent, Santa Clara, CA). The data acquisition and processing were controlled by ChemStation software. The inlet temperature of the gas chromatograph was set to 300 °C. High purity He (99.999%) was employed as the carrier gas. The split ratio is 50:1. The temperature of the transfer line, ion source, and quadrupole mass spectrometer was maintained at 300, 230, and 150 °C, respectively. The mass spectra were acquired in both scan and SIM modes, in which we monitored m/z 256, 292, 326, and 360 for PCBs, m/z 326, 404, 484, 564, and 644 for PBDEs, m/z 153, 166, 178, 202, 228, and 252 for PAHs, and m/z 109, 111, 181, 183, 217, and 219 for HCHs. Naphthalene was employed to measure the column efficiency at 100 °C under the He flow of 1 mL min^{-1}.[39] A commercial HP-5MS capillary column (30 m long × 250 μm i.d.) was employed for comparison (Agilent, Santa Clara, CA).

Five First McReynolds Test Solutes and Their Respective Constants for IRMOFs. As the most widely used system for classifying chromatographic stationary phases, McReynolds constants were used to describe the polarity of the specific IRMOF column using benzene, 1-butanol, 2-pentanone, 1-nitropropane, and pyridine as test solutes.[40] Squalane was used as a standard nonpolar stationary phase, and the McReynolds constants of the IRMOF columns were compared to those of squalane. The McReynolds constants for the IRMOFs are summarized in Table 2. The interactions related to the five selected solutes can be described as follows:[41] X represents benzene, which is related to weak dispersion forces and the polarizability character of the phase. Y represents *n*-butanol, which indicates the hydrogen-bonding ability of the phase. Z represents 2-pentanone, whose behavior relates to the polarizability and part of the dipolar character of the stationary phase. U refers to nitropropane, which is related to the electron donor, electron acceptor, and dipolar character of the phase. S represents pyridine, a strong proton acceptor and polar molecule, which indicates the acidic character of the phase.

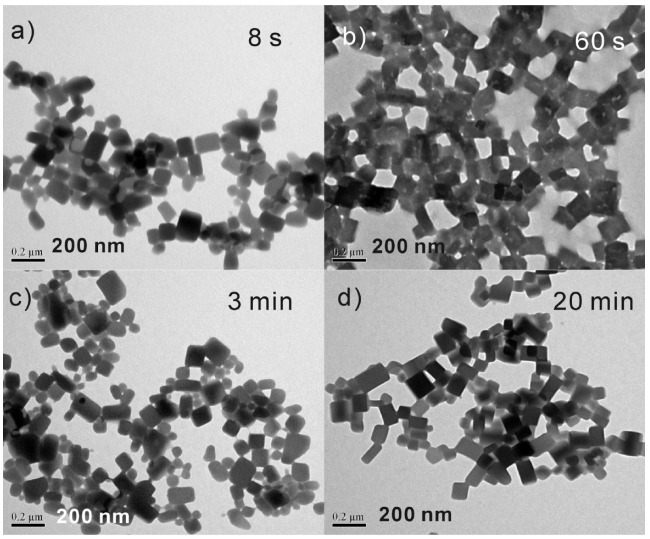

Figure 2. TEM images of the IRMOF-1 prepared by direct mixing of a 10 mL DMF solution of $Zn(OAc)_2 \cdot 2H_2O$ (80 mM) and a 15 mL DMF solution of terephthalic acid (20 mM) with the following reaction times: (a) 8 s; (b) 60 s; (c) 3 min; and (d) 20 min.

Calculation of the Adsorption Enthalpy of Hexachlorobiphenyl (hexa-CB) Isomers on IRMOFs. The adsorption enthalpy for the interaction between the analyte and the stationary phase was calculated from the van't Hoff plot.[14,42,43] Measurements were carried out at 260, 270, 280, 290, and 300 °C on IRMOF-1 and IRMOF-3 capillary columns, respectively. To meet the requirement of zero coverage adsorption at infinite dilution, hexa-CB isomers of 0.016 ng for each were injected onto the column.

RESULTS AND DISCUSSION

Development of a Facile, Rapid, and Robust Approach for Room-Temperature Synthesis of Nanosized IRMOFs. To facilitate preparing IRMOF coated capillary columns for high-resolution separation, we pursued a facile way to synthesize nanosized IRMOFs. A room-temperature direct mixing approach[24] was first tried. However, a direct mixing approach under the same conditions as in the ref 24 gave submicrometer IRMOFs (Figure S1b in the Supporting Information). To make the direct mixing approach possible for rapid synthesis of nanosized IRMOFs, we examined the effect of potential factors, such as the reaction time, molar ratio, and concentration of precursors, on the size and morphology of the IRMOFs. We thus developed a 1-min, room-temperature method to prepare

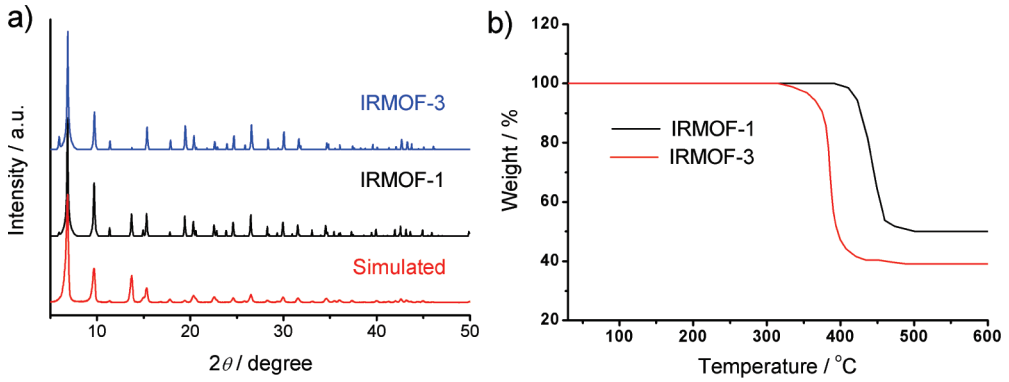

Figure 3. (a) Comparison of the experimental XRD patterns of the evacuated nanosized IRMOF-1 and IRMOF-3 with those simulated. (b) TGA curves of evacuated nanosized IRMOF-1 and IRMOF-3.

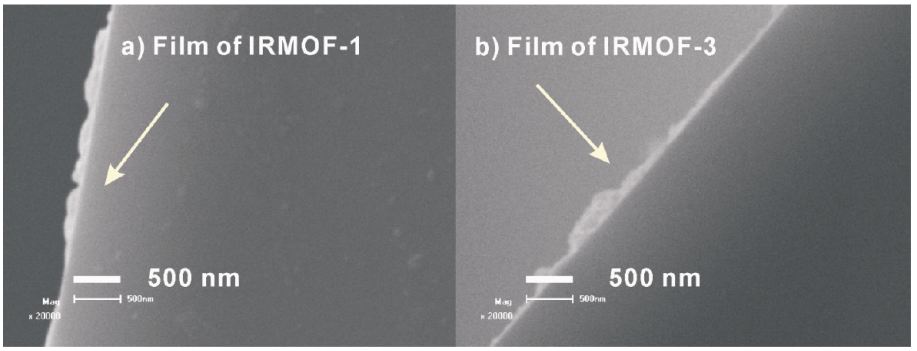

Figure 4. SEM images of the cross-section of the IRMOF coated capillary columns. The thickness of the thin films of (a) IRMOF-1 and (b) IRMOF-3 on the inner walls of the capillary columns was estimated to be 150 ± 50 nm.

well-shaped nanocrystals of IRMOFs without the need for any activation procedures or stabilizing agents.

For a typical preparation of nanosized IRMOF-1, a 10 mL DMF solution of $Zn(OAc)_2 \cdot 2H_2O$ (80 mM) was rapidly poured into a 15 mL DMF solution of terephthalic acid (20 mM) at room temperature (20 °C). The mixture turned turbid immediately, and the IRMOF-1 nanocrystals were thus formed within 1 min. TEM images revealed a crystal size of 80 ± 30 nm for the IRMOF-1 formed in 8 s (Figure 2a). The increase in the reaction time from 8 s to 20 min did not result in a significant change in the size and morphology of the IRMOF-1 (Figure 2). The same is true for the IRMOF-3 (Figure S2 in the Supporting Information).

Control of the molar ratio of $Zn(OAc)_2 \cdot 2H_2O$ to ligand is of great importance for the formation of well-shaped nanosized IRMOFs (Figures S3 and S4 in the Supporting Information). Although the stoichiometry ratio of zinc to ligand is 4:3 for the chemical reaction to form IRMOFs,[27] a molar ratio of 8:3 for zinc acetate to ligand is needed for the successful synthesis of well-shaped nanosized IRMOFs. The concentration of the precursors in the studied range did not have a marked effect on the size and morphology of the IRMOFs as long as the molar ratio of zinc acetate to ligand was kept at 8:3 (Figures S5 and S6 in the Supporting Information). Thus, we can rapidly and robustly synthesize nanosized IRMOFs at room temperature in a flexible scale of reaction time with the precursor concentration at a molar ratio of 8:3 for zinc acetate to ligand with advantages over existing methods.[21,23−36]

The successful synthesis of IRMOF-1 and IRMOF-3 was confirmed by XRD experiments (Figure 3a). Thermogravimetric data showed that the evacuated IRMOF-1 and IRMOF-3 nanocrystals prepared by our 1-min, room-temperature direct mixing approach were stable at 400 and 320 °C, respectively (Figure 3b). The BET surface areas of IRMOF-1 and IRMOF-3 were 2517 and 1957 m^2/g, respectively.

Fabrication of IRMOFs Coated Capillary Columns for High-Resolution GC Separation of POPs. The high thermal stability and porosity of the prepared IRMOFs offer an opportunity to explore their potential as high-resolution separation media for capillary gas chromatography. To show the point of such an application, the IRMOF coated capillary columns were prepared using a dynamic method.[18,19] The SEM images showed thin, solid films of nanosized IRMOFs (150 ± 50 nm thick) on the inner wall of capillary columns, although the direct observation of individual IRMOF nanoparticles was impossible because of the limited resolution of the SEM (Figure 4 and Figures S7 and S8 in the Supporting Information).

To test the high-resolution separation power and applicability of the IRMOF coated capillary columns, 15 PCBs were selected as targets (Table S1 in the Supporting Information), including four groups of isomers: trichlorobiphenyl (tri-CB), tetrachlorobiphenyl (tetra-CB), pentachlorobiphenyl (penta-CB), and hexachlorobiphenyl (hexa-CB). All of the PCBs were baseline separated on an IRMOF-3 coated capillary column (Figure 5a). Meanwhile, the IRMOF-1 coated capillary column also gave a

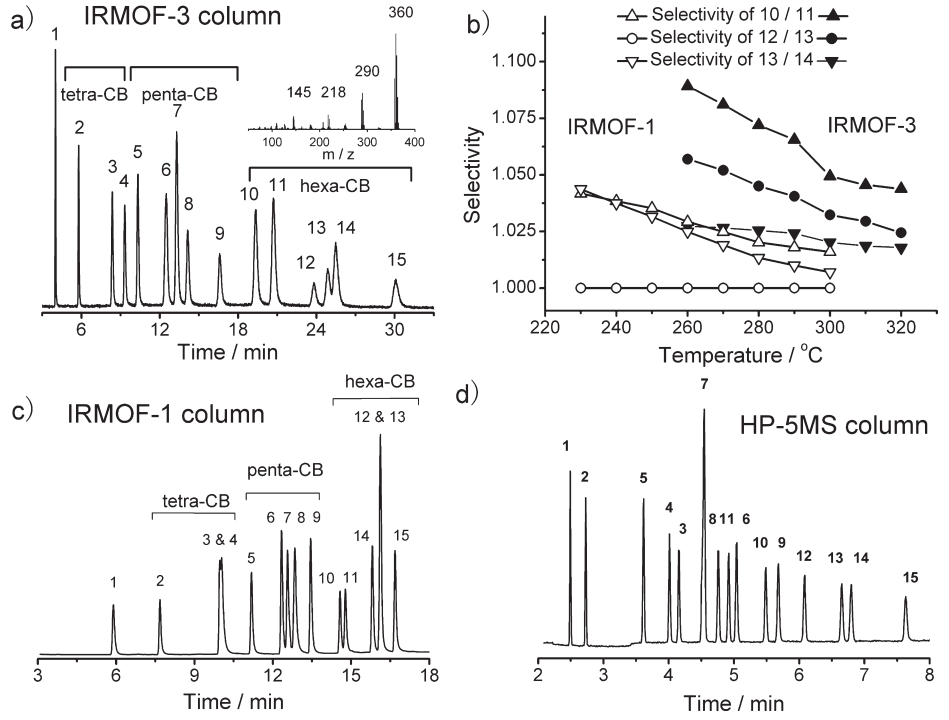

Figure 5. (a) High-resolution gas chromatographic separation of PCBs: 2,4,4′-trichlorobiphenyl (PCB-28, **1**); 2,2′,5,5′-tetrachlorobiphenyl (PCB-52, **2**); 3,3′,4,4′-tetrachlorobiphenyl (PCB-77, **3**); 3,4,4′,5-tetrachlorobiphenyl (PCB-81, **4**); 2,2′,4,5,5′-pentachlorobiphenyl (PCB-101, **5**); 2,3,3′,4,4′-pentachlorobiphenyl (PCB-105, **6**); 2,3′,4,4′,5-pentachlorobiphenyl (PCB-118, **7**); 2,3,4,4′,5-pentachlorobiphenyl (PCB-114, **8**); 3,3′,4,4′,5-pentachlorobiphenyl (PCB-126, **9**); 2,2′,3,4,4′,5′-hexachlorobiphenyl (PCB-138, **10**); 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB-153, **11**); 2,3′,4,4′,5,5′-hexachlorobiphenyl (PCB-167, **12**); 2,3,3′,4,4′,5-hexachlorobiphenyl (PCB-156, **13**); 2,3,3′,4,4′,5′-hexachlorobiphenyl (PCB-157, **14**); and 3,3′,4,4′,5,5′-hexachlorobiphenyl (PCB-169, **15**) on an IRMOF-3 coated capillary column (25 m long × 250 μm i.d.) at 280 °C (the inset shows the mass spectrum obtained for hexa-CB isomers). (b) Selectivity for the separation of hexa-CB on IRMOF-1 and IRMOF-3 coated capillary columns (25 m long × 250 μm i.d.) under different isothermal conditions. (c) High-resolution gas chromatographic separation of PCBs on an IRMOF-1 coated capillary column using a three step temperature program: 180 °C for 2 min, then increasing 5 °C min^{-1} to 290 °C, and finally 290 °C for the remainder of the measurement. (d) High-resolution gas chromatographic separation of PCBs on an HP-5MS capillary column using a three step temperature program: 240 °C for 2 min, then increasing 3 °C min^{-1} to 280 °C, and finally 280 °C for the remainder of the measurement. See Table S1 in the Supporting Information for the structures of the PCBs.

baseline separation of other PCBs, although it could not separate PCB-77 (**3**) from PCB-81 (**4**) and PCB-156 (**13**) from PCB-167 (**12**) (Figure 5c). The chromatogram for the separation of the same PCB mixture on a HP-5MS column is shown in Figure 5d for comparison because HP-5MS is recommended in the EPA-8082A method for the separation of PCBs.[44] IRMOF columns offered good separation efficiency that was generally comparable to that of the HP-5MS column for PCBs in spite of slightly peak tailing and poorer peak width performance than that of the HP-5MS column. In addition, IRMOF-1 and IRMOF-3 coated capillary columns offered a clear group separation of PCB isomers.

It is worth noting that the selectivity of the IRMOF coated capillary columns also depended on temperature as well as the functionality of IRMOFs (Figure 5b). The comparison of the separation of hexa-CB isomers on IRMOF-1 and IRMOF-3 under different isothermal conditions shows that the selectivity for hexa-CB isomers decreased with increasing temperature for a specific IRMOF. Besides, IRMOF-3 with an amino group gave better selectivity for hexa-CB isomers than did IRMOF-1 under identical isothermal conditions (Figure 5b) (see Tables S2−S5 in the Supporting Information for a comparison of retention factors, asymmetry factors, selectivity, and resolution), which is also supported by the measured zero-coverage adsorption enthalpies (Table 1) and McReynolds constants (Table 2). IRMOF-3 showed stronger interaction with five test solutes (larger McReynolds constants) and exhibited higher polarity than did IRMOF-1 (Table 2). Besides, IRMOF-3 offered much larger zero-coverage adsorption enthalpies for hexa-CB isomers than did IRMOF-1 (Table 1), again showing its stronger interaction with hexa-CB isomers. Recently, functionalization with amino groups on MOF MIL-53 (MIL, Matérial Institut Lavoisier) was also found to give an increase in CO_2 zero-coverage adsorption enthalpy.[45]

Table 1. Zero-Coverage Adsorption Enthalpy (Mean ± 95% Confidence Interval, kJ mol^{-1}) for Hexa-CB Isomers on IRMOF-1 and IRMOF-3

	IRMOF-1[a]	IRMOF-3[a]
PCB-138 (**10**)	69.6 ± 1.1	105.8 ± 0.9
PCB-153 (**11**)	70.4 ± 1.1	108.1 ± 1.1
PCB-167 (**12**)	74.0 ± 1.1	110.0 ± 0.9
PCB-156 (**13**)	74.0 ± 1.1	111.7 ± 1.1
PCB-157 (**14**)	72.6 ± 1.1	112.1 ± 1.2
PCB-169 (**15**)	75.5 ± 1.3	115.9 ± 1.3

[a] Measured in the temperature range 260−300 °C.

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Table 2. McReynolds Constants for Nanosized IRMOFs

IRMOFs	X[a]	Y[a]	Z[a]	U[a]	S[a]
IRMOF-1[b]	−79	14	23	−34	−58
IRMOF-3[b]	−32	91	97	17	15

[a] X, Y, Z, U, and S refer to benzene, butanol, 2-pentanone, nitropropane, and pyridine, respectively. [b] Measured at 100 °C.

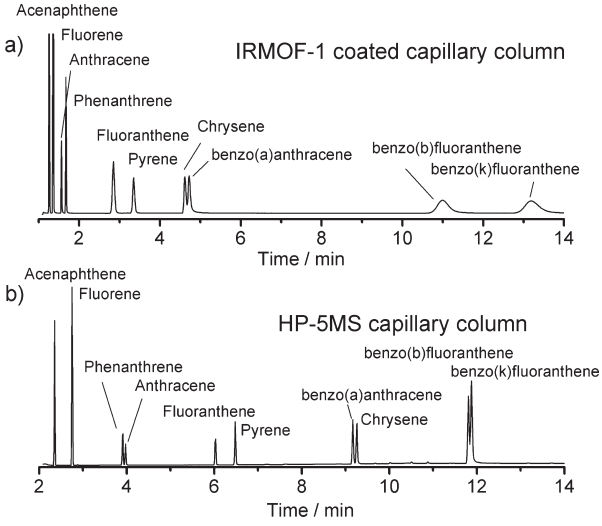

Figure 6. (a) High-resolution separation of PAHs on an IRMOF-1 coated capillary column (25 m long × 250 μm i.d.) at 300 °C. (b) High-resolution separation of PAHs on an HP-5MS capillary column (30 m long × 250 μm i.d.) using a three step temperature program: 200 °C for 2 min, then increasing 10 °C min^{-1} to 280 °C, and finally 280 °C for the remainder of the measurement.

The capability of the IRMOF coated capillary columns was further revealed by high-resolution separation of other environmentally important POPs, that is, PAHs, PBDEs, and HCHs. As shown in Figure 6, IRMOF-1 gave high-resolution separation of several intractable isomer pairs: anthracene/phenanthrene (*Rs* = 3.0), benzo[*a*]anthracene/chrysene (*Rs* = 1.1), and benzo[*b*]fluoranthene/benzo[*k*]fluoranthene (*Rs* = 4.1), which was difficult to be baseline separated on an HP-5MS column (*Rs* = 1.0), although peak broadening for benzo[*b*]fluoranthene and benzo[*k*]fluoranthene was observed on IRMOF-1 because of the constant temperature used for separation. PBDE isomers of BDE-154/BDE-153 and four HCH isomers were also separated from each other on IRMOF-1 (Figure 7).

The high selectivity of such columns likely resulted from the large surface area of the IRMOFs. The adsorption mechanism is dominant on the IRMOFs. The pores of IRMOF-1 and IRMOF-3 should be accessible for all of the molecules in this study because the pore windows of IRMOF-1 (11.2 Å) and IRMOF-3 (9.6 Å) are larger than the size of the largest molecule in our selected targets, benzo[*k*]fluoranthene (6.9 Å × 11.2 Å). Previous reports revealed that if the sizes of the analytes were larger than the size of the pore window, the analytes would be excluded and eluted very quickly.[11,19] However, such a molecular sieving effect was not observed in this study.

The zero-coverage adsorption enthalpies of the PCB isomers on IRMOFs calculated from the van't Hoff plot[14,16,17] (Figure S9) are summarized in Table 1. The elution of the PCB isomers on IRMOF coated capillary columns followed an increasing

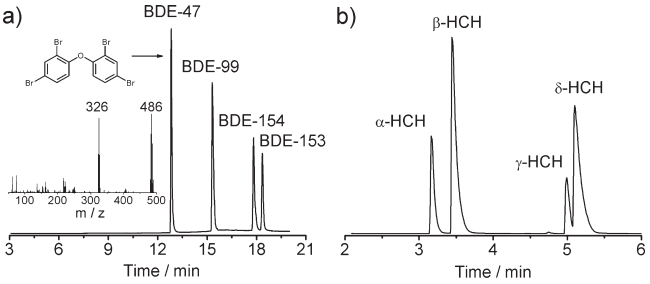

Figure 7. (a) High-resolution gas chromatographic separation of PBDEs on an IRMOF-1 coated capillary column (25 m long × 250 μm i.d.) using a three step temperature program: 180 °C for 2 min, then increasing 5 °C min^{-1} to 310 °C, and finally 310 °C for the remainder of the measurement (inset shows the mass spectrum obtained for BDE-47). (b) High-resolution gas chromatographic separation of HCH isomers on an IRMOF-1-coated capillary column using a three step temperature program: 200 °C for 2 min, then increasing 10 °C min^{-1} to 280 °C, and finally 280 °C for the remainder of the measurement.

order of their adsorption enthalpies. For example, on the IRMOF-1 coated capillary column, six hexa-CB isomers were eluted in an increasing order of PCB-138 (**10**), PCB-153 (**11**), PCB-157 (**14**), PCB-167 (**12**), PCB-156 (**13**), and PCB-169 (**15**) because of their increasing adsorption enthalpies, while PCB-167 (**12**) and PCB-156 (**13**) were not separated from each other because of their identical adsorption enthalpies.

The negative McReynolds constants mainly resulted from the reversed elution order between the probe molecules and alkanes on a standard stationary phase squalene and the IRMOF-1 as a result of their different adsorption enthalpies. For example, benzene eluted between hexane and heptane on a standard stationary phase squalene[40] but eluted before hexane on the IRMOF-1 because of the smaller adsorption enthalpy of benzene (43.9 kJ mol^{-1}) than hexane (46.3 kJ mol^{-1}) on IRMOF-1,[16] resulting in a negative McReynolds constant for benzene (X) on IRMOF-1. Similar negative McReynolds constants were also observed on another novel stationary phase, carbon nanotubes.[43] It should be noted that the McReynolds constants for the IRMOF-1 and IRMOF-3 capillary columns were tested only to provide bulk information about which types of compounds are likely to be retained strongly, but not explicitly to explain the mechanism.

Performance of IRMOF Coated Capillary Columns. The column efficiency of the IRMOF coated capillary columns was measured by employing naphthalene as the test molecule at 100 °C under a He flow of 1 mL min^{-1}.[39] IRMOF-1 and IRMOF-3 coated capillary columns gave the plate values of 2293 and 2063 plates m^{-1}, respectively, indicating good column efficiency, although they offered slightly smaller plate values than a commercial HP-5MS column (2845 plates m^{-1}).

The ability for quantitative and qualitative analysis on IRMOF-1 coated capillary columns was further investigated by changing the mass of the analyte. An increase of the injected target mass resulted in a linear increase of chromatographic peak area, for example, a linear function of $P = 21\,300m + 150\,000$ for PCB-153 with $R = 0.999$, where P denotes peak area (a.u.) and m is the analyte mass (pg) in the range 5−1000 pg (Figure S11 in the Supporting Information). No significant effect of analyte mass on retention time was observed, thereby no change in retention factor in the studied range of analyte mass. This feature of the present IRMOF-1 coated capillary column is favorable for

its application to quantitative analysis. It worth noting that no significant effects of analyte mass on the peak shape and separation efficiency of PCB-153 were observed on the IRMOF-1 coated capillary column. This feature of the IRMOF-1 coated capillary column shows a great advantage over our previous MOF MIL-101 coated capillary column,[18] whose peak shape and separation efficiency were greatly affected by injected analyte mass. The fully coordinated Zn atoms and the symmetric topology in IRMOF-1 are responsible for this feature, which is also supported by its nonpolar nature in the McReynolds test (Table 2). IRMOF coated capillary columns are able to separate samples with quite a few solvents, while other MOF packed or capillary columns are only capable of separation of vapor samples.[13−19]

In addition, a good baseline was observed on the fully conditioned IRMOF-1 and IRMOF-3 capillary columns at 300 °C in the detected mass range from 40 to 700 m/z. The good chromatograms (Figures 5−7 and S12 in the Supporting Information) and high quality mass spectra (Figures 5a, 7a, and S13−S15) were obtained on the IRMOF-1 and IRMOF-3 coated capillary columns by SIM and scan MS detection mode. The relative standard deviation (RSD) for five replicate separations of PAHs is 0.23−0.26% and 2.1−4.5% for retention time and peak area, respectively (Figure S16). The IRMOF-1 coated capillary columns with SIM detection offered a linear range covering three orders of magnitude (Figure S11). These features demonstrate that the IRMOF coated capillary columns are practical for high-resolution separation of POPs under high temperatures.

CONCLUSIONS

In summary, we have reported a facile and robust approach for 1-min, room-temperature synthesis of nanosized IRMOFs with great thermal stability and porosity. The fabricated IRMOF coated capillary columns have been shown to be very promising for separation of POPs with good reproducibility (0.23−0.26% and 2.1−4.5% (RSD) for retention time and peak area, respectively), high resolution (resolutions of 3.0, 1.1, and 4.1 for the intractable isomer pairs anthracene/phenanthrene, benzo[*a*]anthracene/chrysene, and benzo[*b*]fluoranthene/benzo[*k*]fluoranthene on IRMOF-1, respectively), great separation efficiency (theoretical plates of 2293 and 2063 plates m^{-1} for IRMOF-1 and IRMOF-3, respectively), and wide linear range (5−1000 pg for PCB-153 on IRMOF-1).

ASSOCIATED CONTENT

Supporting Information. Additional tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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