Supporting information for

A magnetic covalent organic framework as an adsorbent and a new matrix for enrichment and rapid determination of PAHs and their derivatives in PM$_{2.5}$ by surface-assisted laser desorption/ionization-time of flight-mass spectrometry

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Experimental Section

Chemicals and materials

4 PAHs were purchased from Aldrich Inc., USA (biphenyl, 1 kg; pyrene, 100 g; acenaphthylene, 100 mg) and International Laboratory., USA (phenanthrene, 250 g). 4 NPAHs (1-nitronaphthalene, 3-nitrodibenzofuran, 9-nitroanthracene, 7-nitrobenz[a]anthracene) at 100 µg mL⁻¹ in toluene were purchased from AccuStandard Inc., USA. 4 OHPAHs were purchased from Dr Ehrenstorfer GmbH, Germany (2-hydroxynaphthalene, 0.5 g; 2-hydroxyphenanthrene, 10 mg), AccuStandard Inc., USA (4-hydroxybiphenyl, 100 mg) and Toronto Research Chemicals Inc., USA (3-hydroxyfluorene, 10mg).

Preparation of standard solutions

4 PAHs (biphenyl, pyrene, acenaphthylene and phenanthrene) were dissolved in n-hexane at a concentration of 100 µg mL⁻¹ as stock solutions, respectively. 4 NPAHs (1-nitronaphthalene, 3-nitrodibenzofuran, 9-nitroanthracene and 7-nitrobenz[a]anthracene) have been already in toluene at 100 µg mL⁻¹. 4 OHPAHs (2-hydroxynaphthalene, 2-hydroxyphenanthrene, 4-hydroxybiphenyl and 3-hydroxyfluorene) were prepared in acetonitrile (ACN) at a concentration of 100 µg mL⁻¹ as stock solutions, respectively.

PM$_{2.5}$ sample collection and pre-treatment

Two parallel PM$_{2.5}$ samples were collected at Shanxi University (37º47′42.70″ N, 112º34′52.51″ E) in Taiyuan, China on December 25th, 2017. Two ADS-2062E medium volume air sampler (AMAE (Shenzhen) Co., Ltd, China) and quartz
microfiber filters (Whatman, QMA, 90 mm diameter) were used for PM$_{2.5}$ collection. The flowrate of air samplers was 0.1 m$^3$/min and total sampling period was 23.5 h. After sample collection, the filters were wrapped with aluminum foil and sealed in zip bag at -20 ℃ refrigerator to prevent the photo-degradation.

The whole PM$_{2.5}$ sample filter was cut into strips and extracted by 100 mL hexane/acetone (1:1, v/v) using ultrasonic extraction. Then the organic solvent was dried and converted into 2 mL Milli-Q water. After that, 1 mg Fe$_3$O$_4$@COFs was dispersed into the solution and sonicated for 20 min for enrichment. Next, the Milli-Q water for adsorption was wasted by magnetic separation. 1 mL new Milli-Q water was added, and solution was vortexed until homogeneous. Finally, drop 1 µL uniform sample solution on the MALDI-TOF plate and go to SALDI-TOF-MS analysis with Fe$_3$O$_4$@COFs as matrix directly. The procedures also could be seen in Scheme. S1.

**Enrichment optimization**

To obtain the best enrichment performance of Fe$_3$O$_4$@COFs for target PAHs and their derivatives in PM$_{2.5}$, different ultrasonic enrichment time and nanomaterial dosage were optimized. Mix standard of 4 PAHs, 4 NPAHs and 4 OHPAHs (10 ng for each compound) was used for optimization experiments. The results of the recoveries were determined by GC-MS. The mix standards would be treated by same sample pre-treatments procedures until magnetic separation. After magnetic separation, Fe$_3$O$_4$@COFs were extracted by dichloromethane to elute out PAHs, NPAHs and OHPAHs which were adsorbed by the nanomaterial. The extract would go to GC-MS to determine the recoveries. Both enrichment time (1 – 5 – 10 – 20 – 40
– 60 min) and Fe$_3$O$_4$@COFs dosage (0.1 – 0.25 – 0.5 – 0.75 – 1 mg) were optimized. The dosage was also associated with the SALDI-TOF-MS intensity because after enrichment Fe$_3$O$_4$@COFs would be directly used as matrix in instrumental analysis. Finally, from Fig.S2 and Fig.S3, 20 min (enrichment time) and 1 mg (Fe$_3$O$_4$@COFs dosage) were selected for enrichment.

**Characterization**

S-4800 TEM Scanning electron microscopy (SEM) was obtained from Hitachi, Japan. Tecnai G2 20 200 kV Transmission electron microscopy (TEM) was obtained from FEI Company (Hillsboro, OR, USA). UV-Visible spectrum was obtained by Agilent 8453 UV-Visible spectroscopy with Agilent 89090 temperature controller. Fourier-transform infrared spectroscopy (FT-IR) spectra were obtained using Nicolet 6700 spectrometer (Thermo Fisher, USA).

**Instrumental analysis**

MALDI-TOF-MS analysis was performed on Bruker rapiflex MALDI Tissuetyper mass spectrometer (Bruker Daltonics, Germany) equipped with a nitrogen laser operated in 337 nm. PAHs were detected under positive mode. NPAHs and OHPAHs were analyzed under negative mode.
Scheme S1. Sample pre-treatment procedures using Fe$_3$O$_4$@COFs as enrichment material and matrix (Detailed description was listed in “PM$_{2.5}$ sample collection and pre-treatment” in ESI)
Fig.S1 FT-IR spectra of Fe₃O₄ and Fe₃O₄@COFs
Fig. S2 Enrichment time optimization for PAHs (A), NPAHs (B) and OHPAHs (C) with 1 mg Fe₃O₄@COFs

Fig. S3 Enrichment dosage optimization for PAHs (A), NPAHs (B) and OHPAHs (C) with 20 min enrichment time
Fig.S4 Comparison of MS intensities between with and without Fe$_3$O$_4$@COFs as enrichment material to detect pyrene (A), 7-nitronibenzo[a]anthracene (B) and 2-hydroxybiphenyl (C)
Fig S5 SALDI-TOF-MS spectra of 4 PAHs (a1-a4), 4 NPAHs (b1-b4),

and 4 OHPAHs (c1-c4)
Fig.S6 SALDI-TOF-MS spectra of (a) 100 ng mix standards of PAHs in positive mode; (b) 100 ng mix standards of NPAHs/ OHPAHs in negative mode; (c) Fe₃O₄@COFs blank in positive mode; (d) Fe₃O₄@COFs blank in negative mode; (e) CHCA blank in positive mode; (f) CHCA blank in negative mode
Fig. S7 Calibration curve of pyrene obtained by SALDI-TOF-MS using Fe$_3$O$_4$@COFs as enrichment material and matrix simultaneously.
Fig. S8 Calibration curve of 7-nitrobenz[a]anthracene obtained by SALDI-TOF-MS using Fe$_3$O$_4$@COFs as enrichment material and matrix simultaneously.
Fig. S9 Intensity reproducibilities (n=10) of 10 ng pyrene (a) in positive mode and 10 ng 7-nitrobenz[a]anthracene (b) in negative mode
Table S1. Quantification results of model compounds obtained from SALDI-TOF-MS and GC-MS

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Total amount in 1 µL extract (SALDI-TOF-MS) / ng</th>
<th>Total amount in 1 µL extract (GC-MS) / ng</th>
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<tbody>
<tr>
<td>Pyrene</td>
<td>2.37</td>
<td>2.62</td>
</tr>
<tr>
<td>7-nitrobenz[a]anthracene</td>
<td>0.11</td>
<td>0.07</td>
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