Solid-phase microextraction based on β-ketoenamine-linked covalent organic framework coating for efficient enrichment of synthetic musks in water samples

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Instrumentation

Powder X-ray diffraction (PXRD) patterns were measured with a PANalytical Empyrean diffractometer with Cu K_α radiation (λ=1.5405Å), the fourier transform infrared (FT-IR) spectra were recorded (600-4000 cm^{-1} region) on the Nicolet 710 IR spectrometer. Field-emission scanning electron microscopy (FESEM) micrographs were obtained using a SUPRATM 55 microscope (Carl Zeiss Micro Imaging Co., Ltd., Germany). Thermal gravimetric analysis (TGA) were carried out on an STA 449F3-QMS403C system (Netzsch, Germany) in flowing N_2 within a temperature range of 25°C to 700°C. Nitrogen adsorption and desorption experiments were performed at 77 K on an ASAP2460 (MICROMERITICS, Atlanta, U.S.A).

Synthesis of Tp

A mixture of hexamethylenetetramine (7.4 g, 52.5 mmol), dried phloroglucinol (3 g, 23.8 mmol) and trifluoroacetic acid (45 mL) was stirred in preheated oil bath (100 °C) for 2h under inert atmosphere. Then, 3 M HCl was added to the mixture slowly and the mixture was maintained at 100°C for another 1h, followed by cooling to r.t.. After filtration using Celite bed, obtained filtrate was extracted with dichloromethane (4×100 mL), dried over anhydrous Na2SO4. After evaporation, the orange colored solid was obtained and repeatedly washed with hot ethanol to get the off-white colored powder (0.8 g, yield: 20%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 14.12 (s, 3H, OH), 10.15 (s, 3H, CHO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.2, 173.7, 103.0. MS (EI) m/z 210 (M^+).

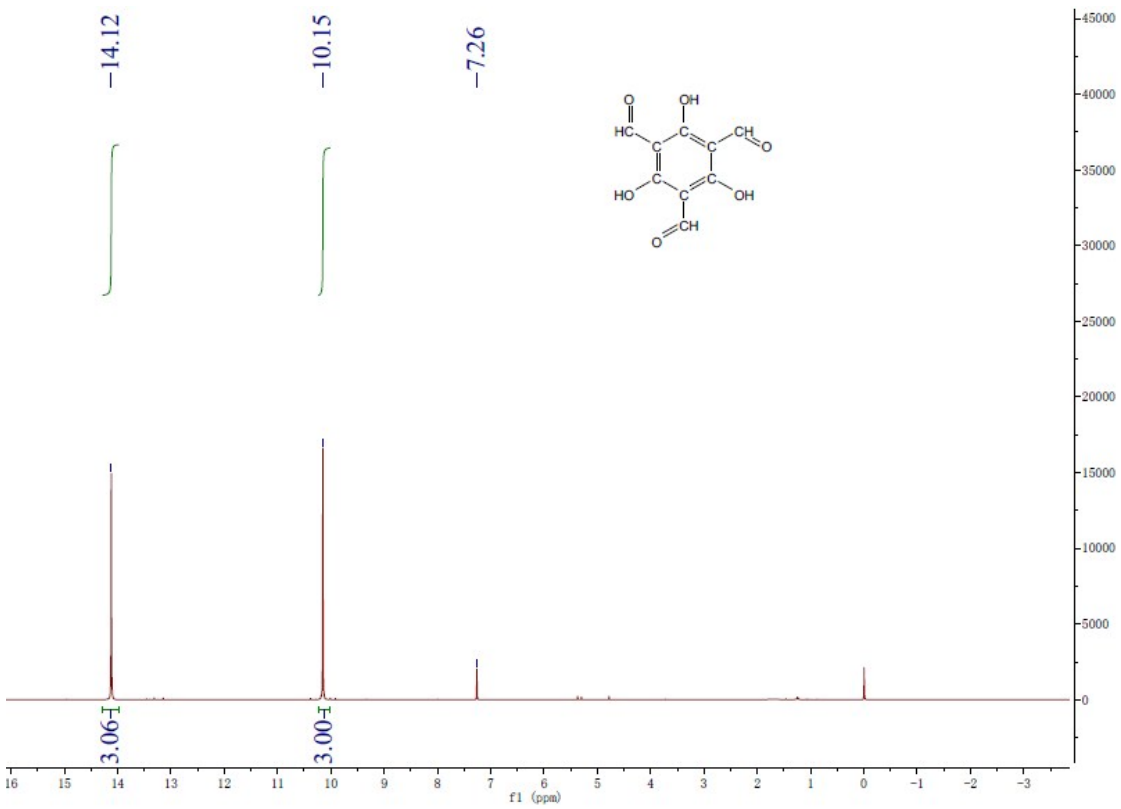


Fig. S1 ^{1}H NMR spectrum of Tp in $CDCl_3$

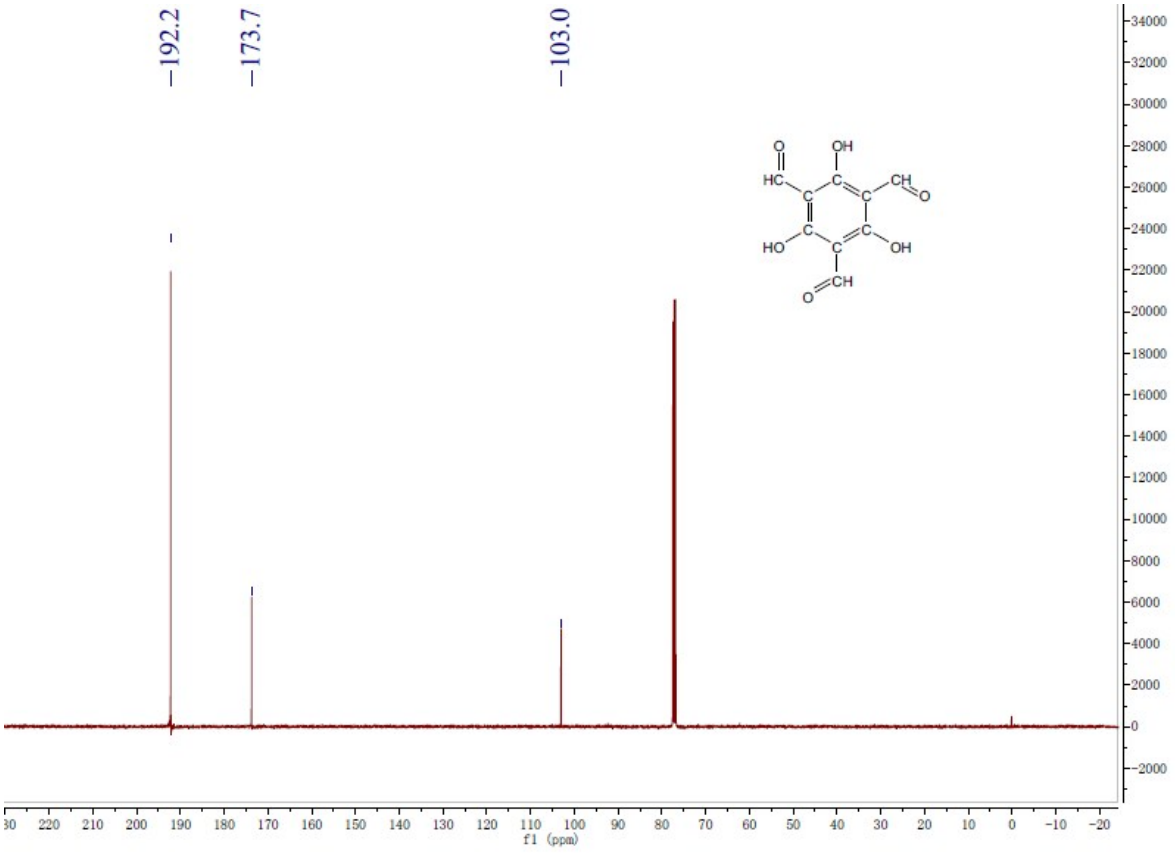


Fig. S2 ^{13}C NMR spectrum of Tp in $CDCl_3$

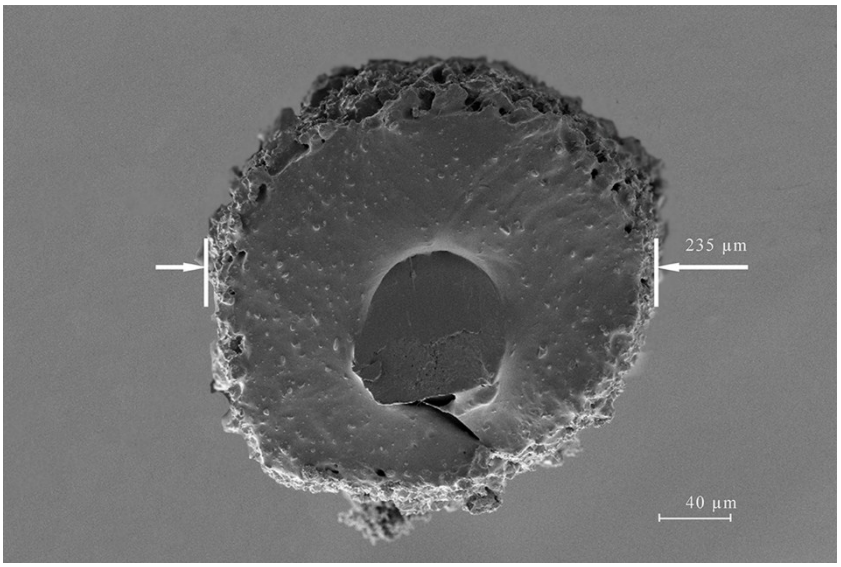


Fig. S3 The cross-sectional SEM images of the TpPa-1-coated fiber.

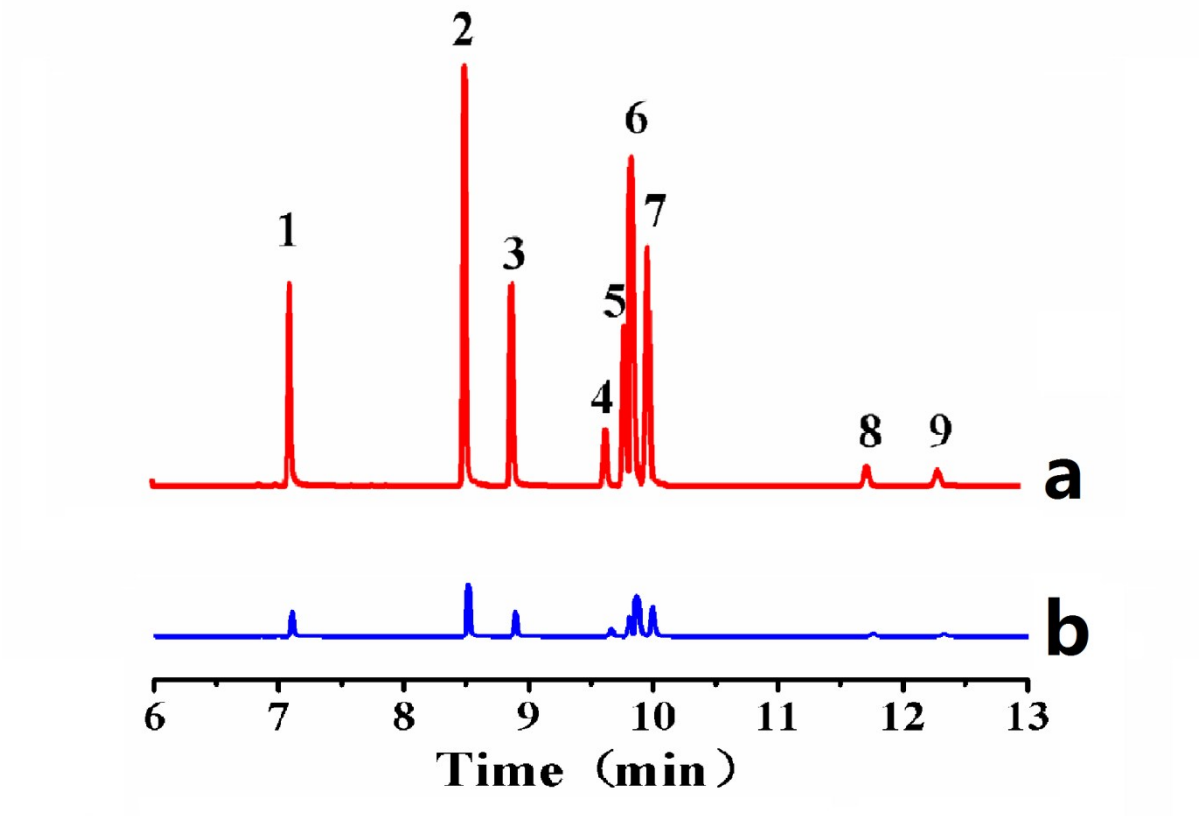
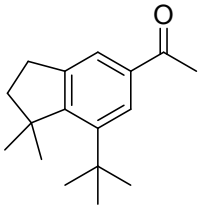
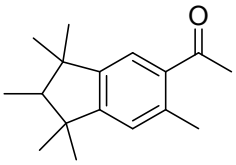
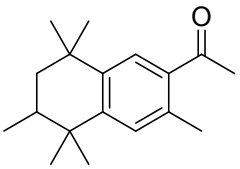
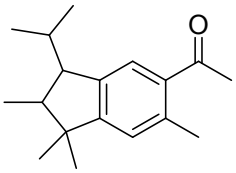
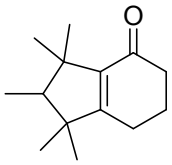
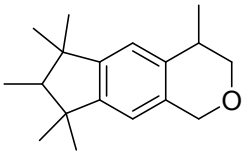
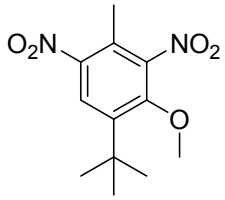
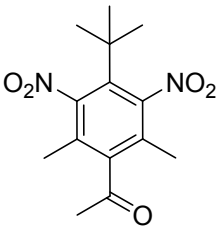
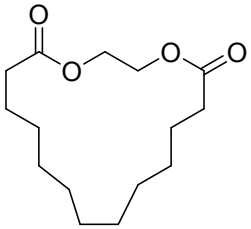


Fig. S4 Chromatograms for the nine synthetic musks (initial concentration = 1μg·L^{-1}) after SPME of using TpPa-1-coating (a) and glued coating (b).

Table S1 Chemical structure, physical–chemical properties and EFs value of synthetic musks.

Analytes	Chemical Structure	Boiling point (°C)	log K_{ow}	EFs
ADBI		309.1	6.6	5436 ± 15
AHMI		336.6	6.7	4791 ± 16
AHTN		356.8	5.7	6143 ± 60
ATII		350	8.1	6254 ± 7
DPMI		286.1	4.9	1214 ± 42
HHCB		356.8	5.9	4960 ± 19

Musk ambrette		369.3	5.7	12487 ± 9
Musk ketone		436	4.3	6229 ± 24
Musk NN		138-142 (1 mm Hg)	4.7	1642 ± 18