Supporting Information

Facile preparation of a cationic COF functionalized magnetic nanoparticle and used for the determination of nine hydroxylated polycyclic aromatic hydrocarbons in smokers' urine

Wenfen Zhang [a,f†], Yanhao Zhang [b†], Guangrui Zhang [a], Jiying Liu [a], Wuduo Zhao *[c], Wenjing Zhang [a], Kai Hu [d], Fuwei Xie[e], Shusheng Zhang [a]*

[a.] College of Chemistry and Molecular Engineering, Zhengzhou University, Kexue Avenue 100, Zhengzhou, Henan 450001, P. R. China.

[b.] State Key Laboratory of Environmental and Biological Analysis, Department of Chemistry, Hong Kong Baptist University, Hong Kong, 999077

[c.] Center of Advanced Analysis and Computational Science, Key Laboratory of Molecular Sensing and Harmful Substances Detection Technology, Zhengzhou University, Kexue Avenue 100, Zhengzhou, Henan 450001, P. R. China.

[d.] Henan University of Traditional Chinese Medicine, Zhengzhou, Henan 450001, P. R. China.

[e.] Zhengzhou Tobacco Research Institute of CNTC, Fengyang Street 2, Zhengzhou, Henan 450001, P. R. China.

[†.] These authors contribute equally and should be considered co-first authors.

***Corresponding authors at:**

Shusheng Zhang: Email: zsszz@126.com, Telephone number: +8613513801442, Fax:+860 371 67763224.

Wuduo Zhao: Email: zhaowuduo@163.com, Telephone number: +8613607675532, Fax: +86 0371 67763224.

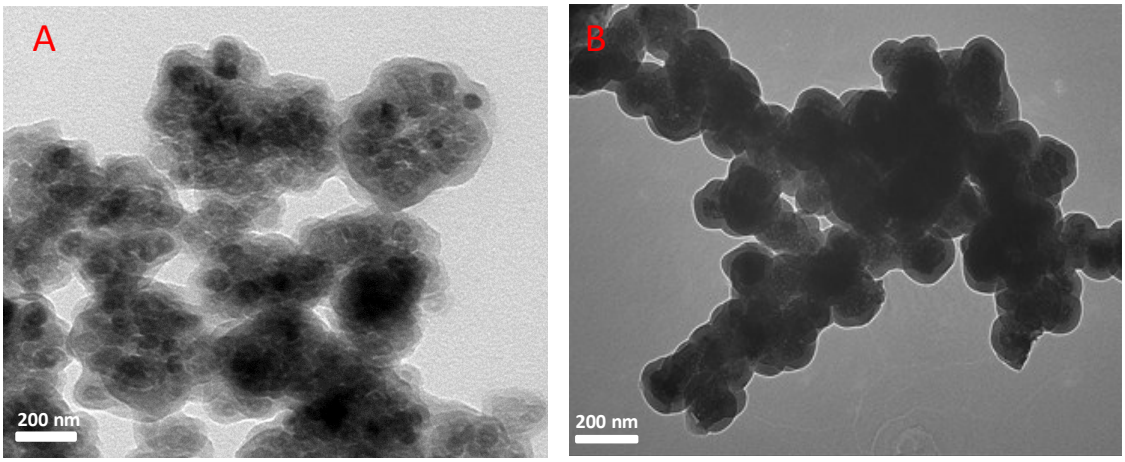

Fig. S1 The TEM of Fe_3O_4@SiO_2 prepared using different amount of TEOS: A, 1mL TEOS; B, 2mL TEOS

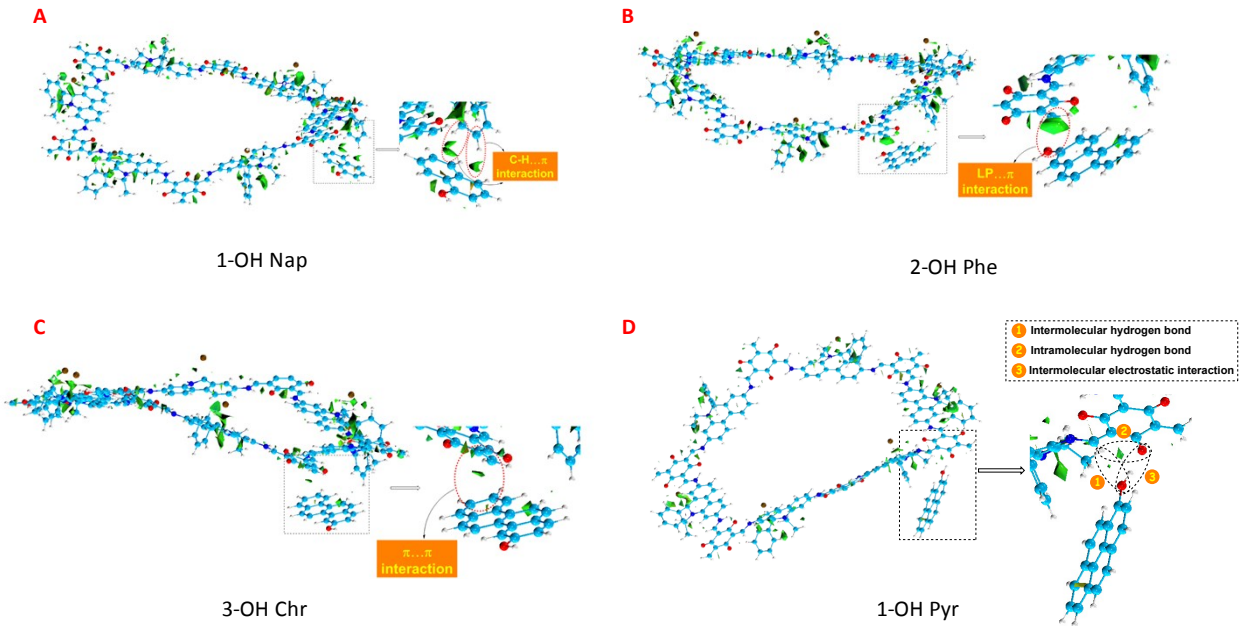

Fig. S2 The representation non-covalent interaction simulation between EB COF and OH-PAHs.

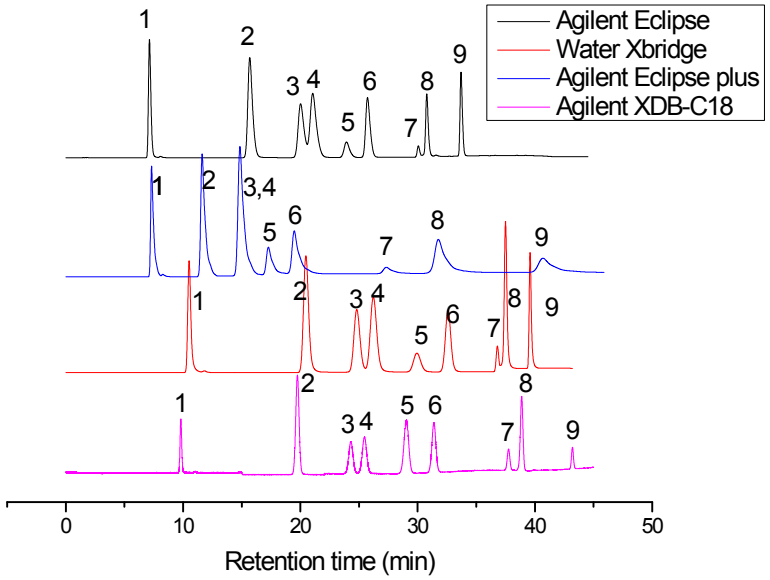

Fig. S3 The chromatogram of 9 OH-PAHs based on different column. Peaks:1, 1-OH Nap; 2, 2-OH Flu; 3, 2-OH Phe; 4, 3-OH Phe; 5, 9-OH Phe; 6, 4-OH Phe; 7, 3-OH FA; 8, 1-OH Pyr; 9, 3-OH Chr.

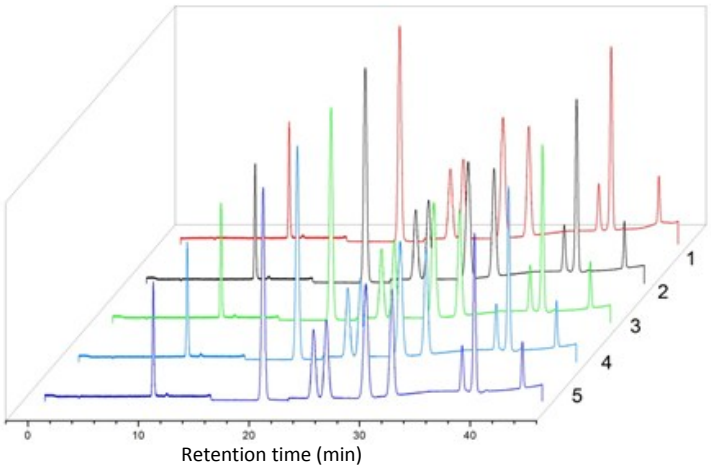

Fig. S4 The stability of the established separation method

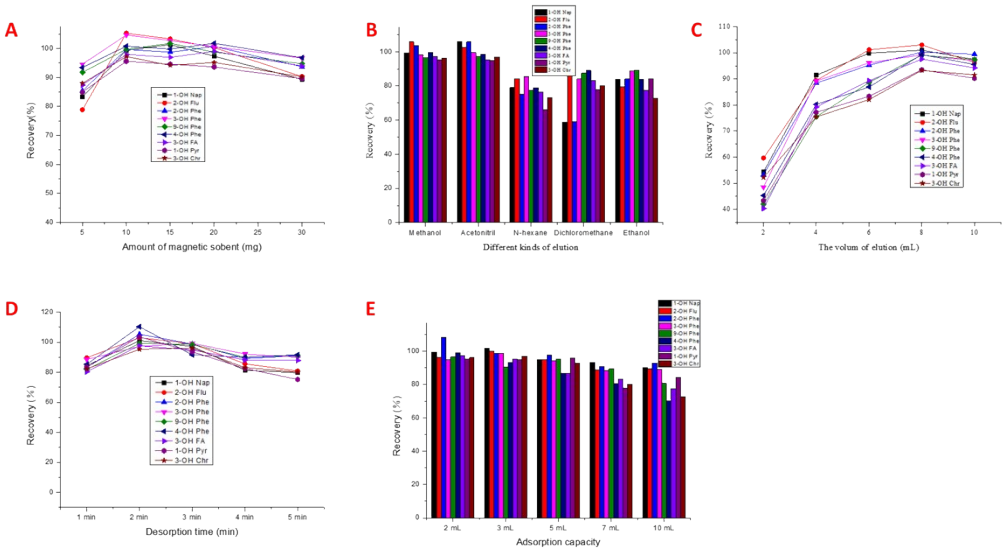

Fig. S5 Effect of experimental parameters on the MSPE efficiency of OH-PAHs (A, Amount of magnetic sorbent vs recovery; B, The kinds of elution vs recovery; C, The volume of elution vs recovery; D, Desorption time vs recovery; E, Adsorption capacity vs recovery)

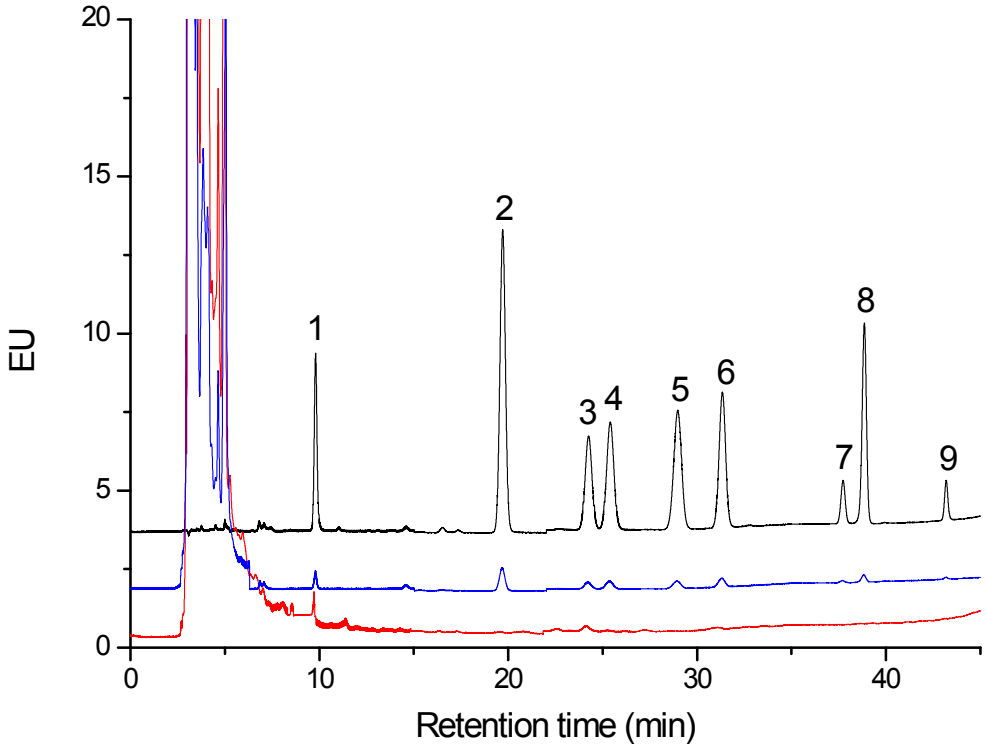

Fig. S6 Typical chromatograms of OH-PAHs in the urine samples of the smokers. Peaks: 1, 1-OH Nap; 2, 2-OH Flu; 3, 2-OH Phe; 4, 3-OH Phe; 5, 9-OH Phe; 6, 4-OH Phe; 7, 3-OH FA; 8, 1-OH Pyr; 9, 3-OH Chr.

Table S1 The information of the volunteers participating in this projects

Smokers	height	weight	heartrate	age	cigarettes/day	Smoke age
Low Tar level						
1	163.5	63.0	76	54	10	18
2	176.0	67.0	72	22	10	2
3	164.0	87.0	76	23	10	2
4	165.0	60.0	98	58	15	30
5	170.0	61.0	85	30	20	14
6	158.5	57.0	90	38	15	8
7	158.5	69.0	76	47	15	27
8	170.0	51.0	85	26	15	9
9	174.5	66.0	78	47	20	31
10	170.0	61.0	71	50	12	28
11	163.5	57.0	73	41	20	21
12	172.0	75.0	81	30	10	21

13	167.0	74.0	88	22	10	10
14	166.0	56.0	85	26	10	4
15	174.0	67.0	80	51	17	30
16	160.0	60.0	85	48	15	28
17	171.5	81.0	80	51	15	34
18	170.0	65.0	78	42	20	15
19	164.0	87.0	107	36	17	20
20	163.5	63.0	76	54	10	18
Medium Tar level						
21	160.5	62.0	100	45	13	25
22	163.5	53.0	70	25	10	8
23	170.0	72.0	96	44	14	Unknow
24	171.0	72.0	90	48	18	29
25	160.0	40.0	84	51	10	39
26	173.0	54.0	82	43	10	26
27	164.0	65.5	80	50	10	17
28	163.0	74.5	88	42	10	24
29	158.0	52.0	93	58	12	22
30	164.0	50.6	88	54	15	25
31	162.5	59.5	90	27	20	7
32	165.7	64.5	83	43	20	27
33	162.0	74.0	88	46	20	24
34	153.0	54.0	78	53	20	33
35	170.0	61.0	84	42	10	8
36	179.0	76.0	76	32	10	18
37	173.0	64.0	90	33	10	21
38	172.0	81.0	84	58	20	40
39	164.0	60.0	86	60	20	41
40	182.0	60.0	90	19	20	3
High Tar level						
41	171.0	72.0	98	22	15	5
42	175.0	105.0	86	31	20	18
43	166.0	60.0	68	44	15	22
44	163.0	63.5	81	25	14	11
45	169.0	64.0	78	57	15	34
46	164.5	62.5	74	64	14	36
47	159.0	69.0	84	51	40	35
48	164.0	63.0	82	65	15	38
49	163.0	66.0	82	50	10	30
50	162.0	59.0	86	57	20	30
51	164.0	63.0	88	37	15	18
52	174.0	71.0	82	22	20	5
53	156.5	61.5	72	61	10	37
54	181.0	96.5	86	26	25	12
55	161.0	60.5	70	58	20	44

56	180.0	72.0	85	49	20	31
57	182.0	75.0	78	22	15	1
58	178.0	72.0	80	51	10	30
59	165.0	61.0	96	26	20	15
60	156.5	67.5	103	49	16	23
Non-smokers						
61	159.0	69.0	65	31	--	--
62	171.5	74.0	64	56	--	--
63	172.0	68.0	74	42	--	--
64	170.0	75.5	66	23	--	--
65	169.0	64.0	60	27	--	--
66	173.0	75.0	82	37	--	--
67	153.0	53.0	76	46	--	--
68	162.5	52.0	72	58	--	--
69	163.0	63.0	78	42	--	--
70	174.0	78.0	69	41	--	--
71	174.5	55.0	96	32	--	--
72	166.0	69.5	60	60	--	--
73	178.0	76.5	68	27	--	--
74	162.0	56.0	81	26	--	--
75	162.6	70.5	83	32	--	--
76	164.0	68.0	78	52	--	--
77	160.0	58.0	83	58	--	--
78	166.0	56.5	85	26	--	--
79	168.0	54.5	71	47	--	--
80	156.0	55.0	72	55	--	--

Table S2 Calibration curves in matrix and pure solvent

Probes	Calibrations in matrix	R^2	Calibrations in pure solvent	R^2	slope ratios
1-OH NA	y = 34714x + 49162	0.9965	y = 35872x + 34840	0.9998	0.9677
2-OH FLU	y = 126667x + 98304	0.9996	y = 113920x + 89807	0.9996	1.112
2-OH PHE	y = 51158x + 43213	0.9992	y = 53813x + 53651	0.9999	0.9507
3-OH PHE	y = 61671x + 39215	0.9993	y = 65309x + 11448	0.9997	0.9443
9-OH PHE	y = 85615x - 28025	0.9999	y = 90319x + 31451	0.9998	0.9479
4-OH PHE	y = 71958x + 8865.5	0.9998	y = 69329x + 7228	0.9997	1.038
3-OH FA	y = 16828x - 13810	0.9995	y = 15814x - 13160	0.9994	1.064
1-OH P	y = 63008x + 19637	0.9998	y = 66307x + 19932	0.9990	0.9502
3-OH CHR	y = 14629x - 7263.1	0.9995	y = 13546x + 9246	0.9997	1.080