Electronic Supplementary Material

Room temperature in-situ preparation of hydrazine-linked covalent organic frameworks coated capillaries for separation and determination of polycyclic aromatic hydrocarbons

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The synthesis of 1,3,5-tris(4-formylphenyl)benzene was referenced from the literature [1] with some slight changes as shown in Figure S1. 1,3,5-tribromobenzene (0.5 g, 1.55 mmol), 4-formylphenylboronic acid (1.1 g, 6.95 mmol), potassium carbonate (1.05 g, 7.5 mmol) and tetra (triphenylphosphine)palladium (0.085 g, 0.075 mmol) were added to a 100 mL round-bottom flask protected with N_2, followed by a mixture of toluene (25 mL), ethanol (5 mL) and water (5 mL) at reflux for 48 h. The reaction was detected by thin-layer chromatography to see if the reaction was finished. The filtrate was extracted with CH_2Cl_2, and the obtained CH_2Cl_2 phase was dried with anhydrous $MgSO_4$, and then the solvent was evaporated by spin evaporation, and the obtained crude product was purified by SiO_2 column chromatography, and the eluent was CH_2Cl_2.

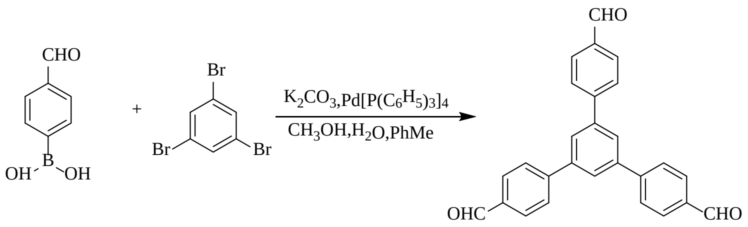


Figure S1. Synthesis of 1,3,5-tris(4-formylphenyl)benzene

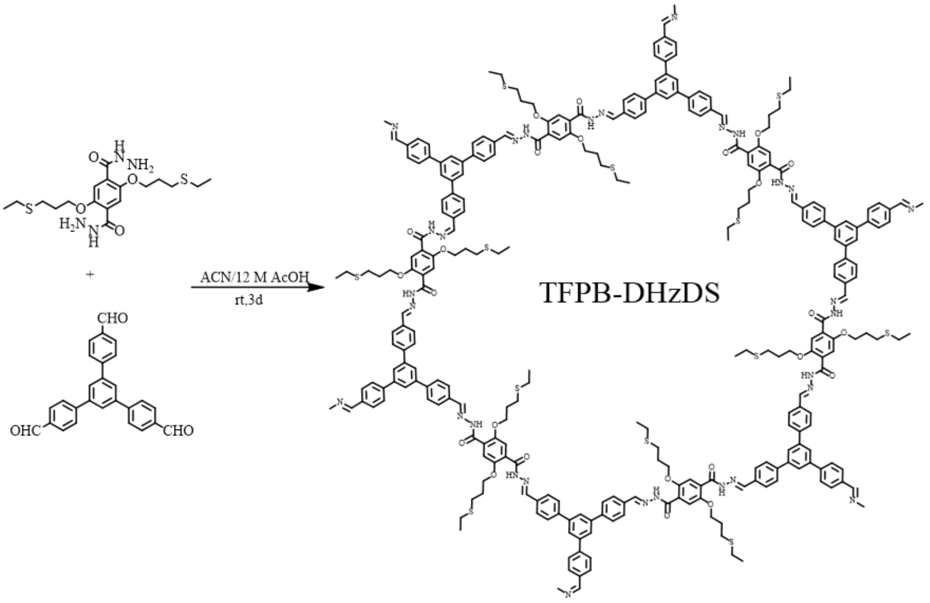


Figure S2. Synthesis of TFPB-DHzDS under the room temperature.

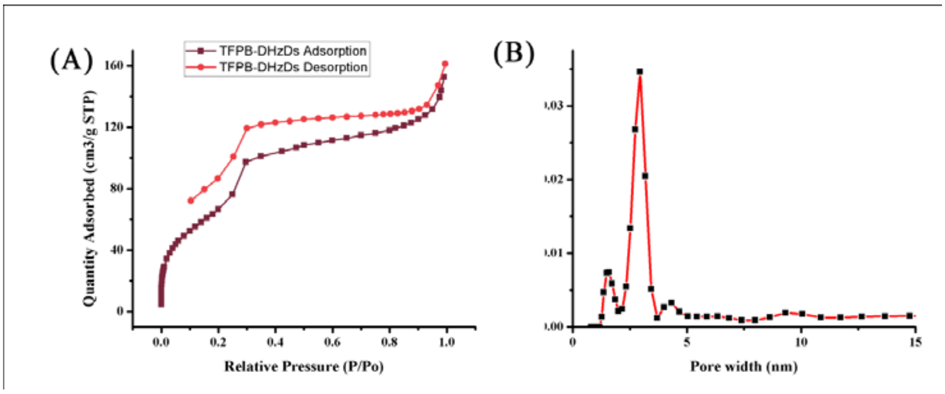


Figure S3. (A) N_2 adsorption and desorption isotherm profiles of TFPB-DHzDs measured at 77 K; (B) Pore size distribution of TFPB-DHzDs calculated by the BJH method based on the adsorption isothermal.

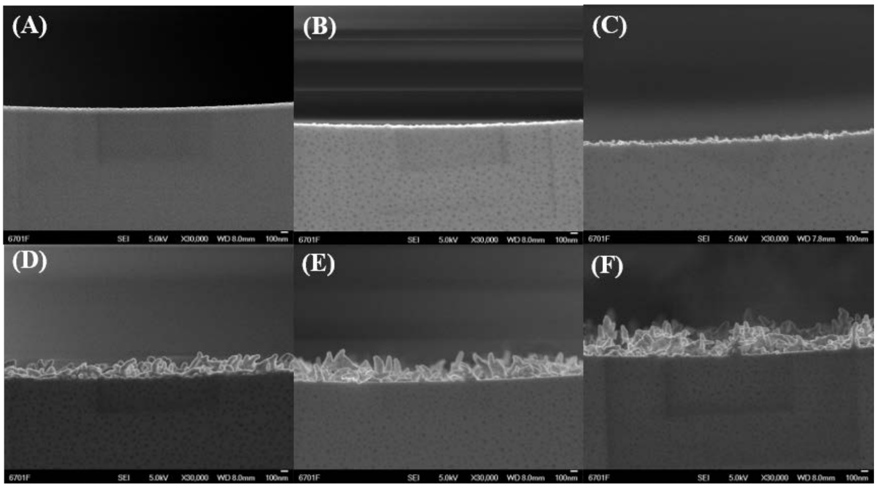


Figure S4. SEM images of cross-sections of COF TFPB-DHzDS coated capillaries prepared at different pass-through monomer concentrations. (A) bare capillary; (B) 0.5 mg/mL; (C) 1.0 mg/mL; (D) 2.0 mg/mL; (E) 4.0 mg/mL; (F) 8.0 mg/mL

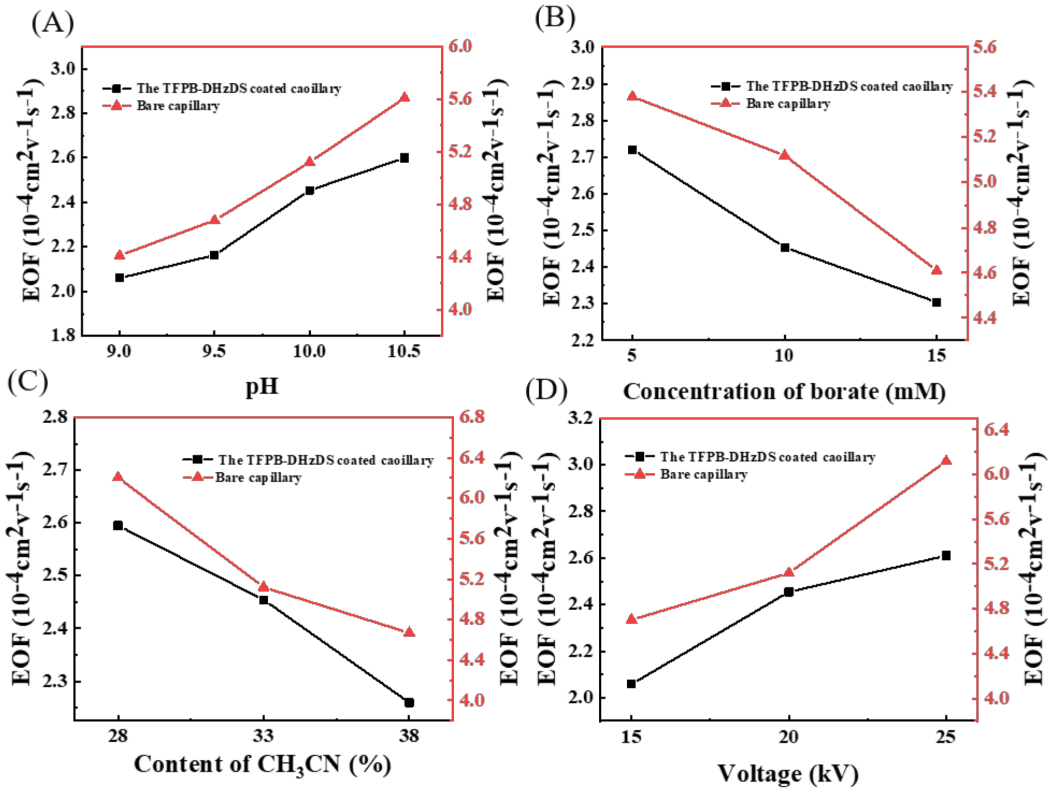


Figure S5. Comparison of EOF in the bare capillary and the COF TFPB-DHzDS capillaries with pH of buffer solution (A), borax concentration (B), acetonitrile content (C) and voltage (D)

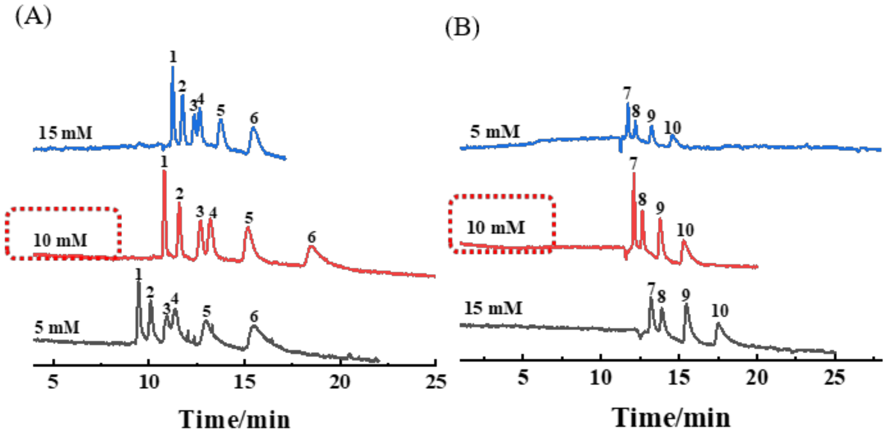


Figure S6. Effect of borax concentration on the separation of two groups PAHs; Conditions: 5-15 mM borax, pH=10.00, +20 kV, 32.5% acetonitrile for (A); 5-15 mM borax, pH=10.50, +20 kV, 45.0% acetonitrile for (B). Spectral peak designation: 1. NAP; 2. ANA; 3. ANT; 4. PHE; 5. PYR; 6. BPH; 7. FLU; 8. FLT; 9. BaA; 10. BbF.

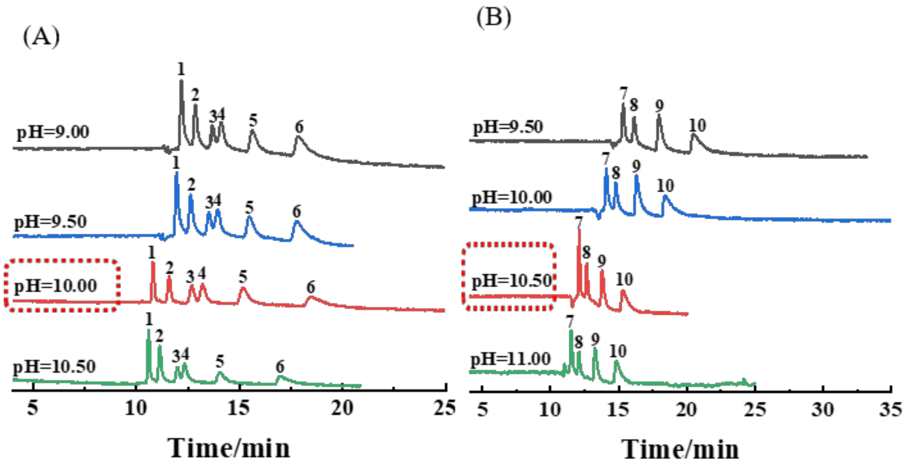


Figure S7. Effect of buffer solution pH value on the separation of two groups PAHs. Conditions: 10 mM borax, pH=9.00-10.50, +20 kV, 32.5% acetonitrile for (A); 10 mM borax, pH=9.50-11.00, +20 kV, 45.0% acetonitrile for (B). Other conditions are same as Figure S6.

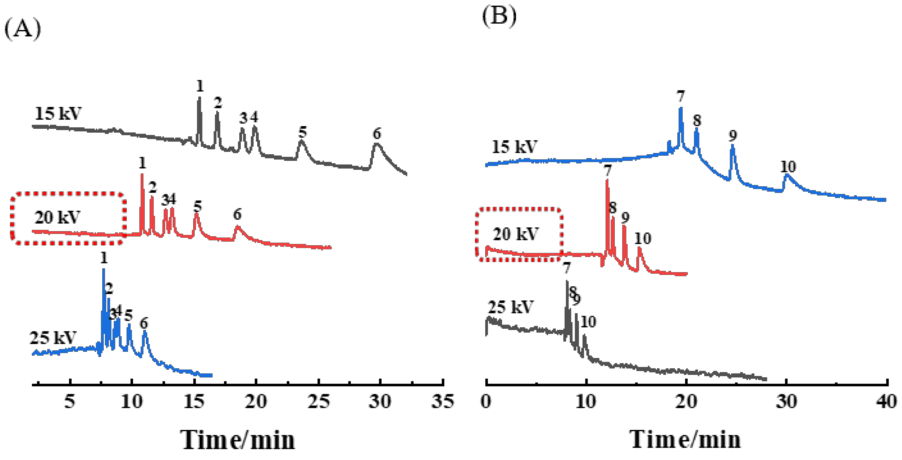


Figure S8. Effect of voltage on the separation of two groups PAHs. Conditions: 10 mM borax, pH=10.00, +15 kV - +25 kV, 32.5% acetonitrile for (A); 10 mM borax, pH=10.50, +15 kV - +25 kV, 45.0% acetonitrile for (B). Other conditions are same as Figure S6.

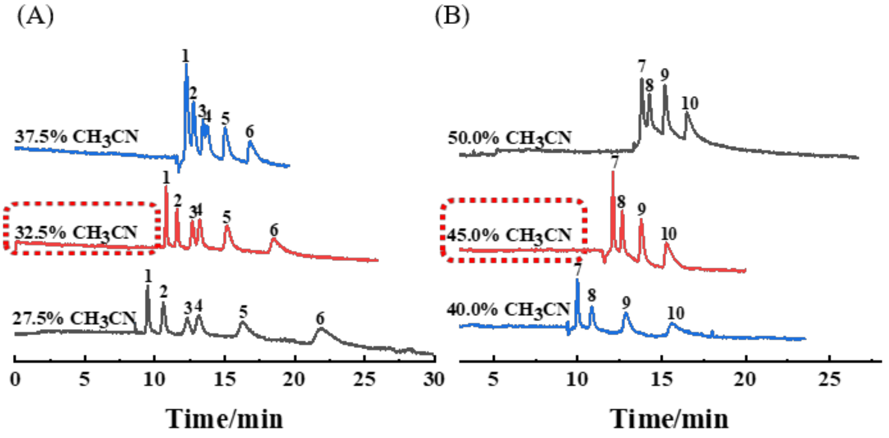


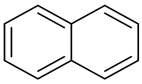
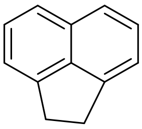
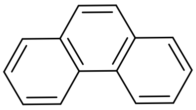
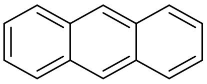
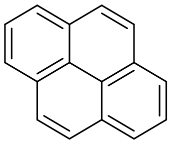
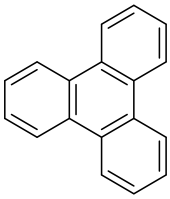
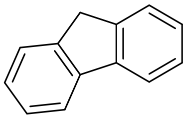
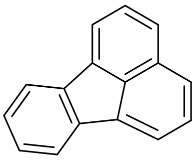
Figure S9. Effect of acetonitrile content in buffer solution on the separation of two groups PAHs. Conditions: 10 mM borax, pH=10.00, +20 kV, 27.5%-37.5% acetonitrile for (A); 10 mM borax, pH=10.50, +20 kV, 40.0%-45.0% acetonitrile for (B). Other conditions are same as Figure S6.

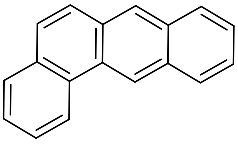
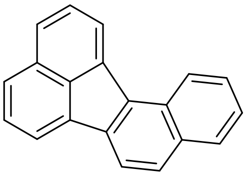
Table S1 The chromatographic data of the two groups PAHs under optimum separation conditions.

Analytes	Capacity factor	Asymmetry	N (×10^4, plates/m)	R_s

1	NAP	1.00	1.29	1.11	$R_{s1,2}=1.53$
2	ANA	1.15	1.44	0.58	$R_{s2,3}=1.93$
3	ANT	1.35	1.40	0.92	$R_{s3,4}=0.85$
4	PHE	1.45	1.65	0.57	$R_{s4,5}=1.73$
5	PYR	1.81	2.53	0.15	$R_{s5,6}=1.75$
6	BPH	2.43	3.09	0.11	
7	FLU	0.87	1.23	1.62	$R_{s7,8}=1.48$
8	FLT	0.95	1.36	1.98	$R_{s8,9}=2.07$
9	BaA	1.13	2.14	0.56	$R_{s9,10}=1.46$
10	BbF	1.36	4.76	0.22	

Table S2 Relative information of two groups PAHs

Analytes	Chemical structure	LogK_{ow}[a]	Size (Å)[b]	Volume (Å^3)[c]
NAP		3.05	4.97-7.19	457.00
ANA		3.48	5.96-7.16	521.51
PHE		4.05	5.56-9.28	577.24
ANT		4.05	4.98-9.53	583.41
PYR		4.37	7.01-8.94	593.82
BPH		5.05	8.03-9.27	690.94
FLU		3.77	4.99-9.04	558.09
FLT		4.37	6.05-9.03	628.76

BaA		5.05	6.00-11.50	703.10
BbF		5.37	7.15-11.02	745.51

[a] logK_{OW} came from SciFinder

[b] The molecular size calculated with Accelrys Discover Studio Client.

[c] The molecular volume calculated with HyperChem.

Table S3 Relative standard deviations of peak time and peak area of ten PAHs

Analytes	Intra-day (n=3)		Inter-day (n=3)		Column-to-column (n=3)	
	t[a] (%)	A[b] (%)	t[a] (%)	A[b] (%)	t[a] (%)	A[b] (%)
NAP	1.09	0.80	2.08	4.65	2.12	3.07
ANA	0.91	3.57	2.34	4.40	2.34	9.47
ANT	0.97	2.39	2.67	3.48	2.87	3.84
PHE	1.05	0.07	2.71	4.87	3.05	5.54
PYR	1.75	4.13	3.59	2.82	3.66	4.99
BPH	2.79	3.56	4.41	4.71	3.13	4.21
FLU	0.64	3.36	1.12	4.04	2.91	3.57
FLT	0.50	0.10	1.58	2.91	3.04	4.54
BaA	1.08	3.83	2.49	3.56	3.68	7.60
BbF	2.41	3.53	3.89	1.38	5.29	4.56

a RSD of migration time.

b RSD of peak area.

Table S4 Detection of ten PAHs in Yellow River water samples

Sample	Analytes	Original amount (μg/mL)	Spiked amount (μg/mL)	Determined amount (μg/mL)	Recovery (%)
Yellow River Water	NAP	ND[a]	5.0	5.1	101.7
			25.0	27.3	109.2
			50.0	54.8	109.6
	ANA	ND[a]	5.0	5.4	108.4
			25.0	27.5	109.9
			50.0	54.6	109.2

	ANT	ND[a]	5.0	5.5	109.2
			25.0	25.1	100.4
			50.0	47.0	93.97
	PHE	ND[a]	5.0	4.8	96.62
			25.0	26.8	107.3
			50.0	52.1	104.1
	PYR	ND[a]	5.0	5.0	99.09
			25.0	25.4	101.5
			50.0	50.2	100.4
	BPH	ND[a]	5.0	4.8	95.45
			25.0	25.0	100.1
			50.0	52.7	105.4
	FLU	ND[a]	5.0	4.5	90.98
			25.0	24.7	98.97
			50.0	54.3	108.6
	FLT	ND[a]	5.0	4.6	92.23
			25.0	25.7	103.0
			50.0	52.3	104.6
	BaA	ND[a]	5.0	4.5	90.97
			25.0	26.4	105.5
			50.0	52.0	103.9
	BaF	ND[a]	5.0	4.8	96.30
			25.0	22.5	90.11
			50.0	45.5	90.91

[a] Not detected

Table S5 Detection of ten PAHs in Soil on the bank of the Yellow River

Sample	Analytes	Original amount (μg/mL)	Spiked amount (μg/mL)	Determined amount (μg/mL)	Recovery (%)
Soil on the bank of the Yellow River	NAP	ND[a]	5.0	4.8	95.18
			25.0	23.9	95.44
			50.0	52.2	104.4
	ANA	ND[a]	5.0	5.4	108.9
			25.0	22.5	90.15
			50.0	54.3	108.7
	ANT	ND[a]	5.0	5.5	109.0
			25.0	22.7	90.88
			50.0	49.6	99.12
	PHE	ND[a]	5.0	4.7	93.69
			25.0	23.5	93.96
			50.0	50.6	101.2
	PYR	ND[a]	5.0	4.6	92.21

			25.0	23.1	92.47
			50.0	45.0	90.01
	BPH	ND[a]	5.0	4.6	92.70
			25.0	22.9	91.54
			50.0	45.9	91.80
	FLU	ND[a]	5.0	4.7	93.31
			25.0	27.0	107.9
			50.0	54.8	109.6
	FLT	ND[a]	5.0	4.7	93.62
			25.0	23.0	92.09
			50.0	54.2	108.4
	BaA	ND[a]	5.0	4.6	92.69
			25.0	22.7	90.62
			50.0	52.3	104.5
	BaF	ND[a]	5.0	4.8	96.26
			25.0	25.8	103.3
			50.0	50.9	101.9

[a] Not detected

Table S6 Detection of ten PAHs in Fountain water on campus

Sample	Analytes	Original amount (μg/mL)	Spiked amount (μg/mL)	Determined amount (μg/mL)	Recovery (%)
Fountain water on campus	NAP	ND[a]	5.0	4.9	97.43
			25.0	26.3	105.1
			50.0	49.2	98.45
	ANA	ND[a]	5.0	5.3	106.8
			25.0	27.5	110.0
			50.0	54.8	109.6
	ANT	ND[a]	5.0	5.4	107.9
			25.0	24.1	96.52
			50.0	52.2	104.3
	PHE	ND[a]	5.0	4.9	98.01
			25.0	24.9	99.71
			50.0	49.5	98.91
	PYR	ND[a]	5.0	5.0	99.87
			25.0	26.1	104.5
			50.0	47.1	94.17
	BPH	ND[a]	5.0	5.0	100.7
			25.0	23.8	95.19
			50.0	52.5	105.0
	FLU	ND[a]	5.0	5.0	99.71
			25.0	24.7	98.90

		50.0	55.5	111.0
FLT	ND[a]	5.0	4.7	94.93
		25.0	26.8	107.2
		50.0	53.2	106.4
BaA	ND[a]	5.0	4.6	91.43
		25.0	23.9	95.40
		50.0	52.1	104.2
BaF	ND[a]	5.0	4.9	97.37
		25.0	23.0	92.16
		50.0	47.3	94.51

[a] Not detected

Apparatus and Reagents

The ultra-pure water was purified through 18,202V AXL water purification system (Chongqing, China). The powder X-ray diffraction (PXRD) of TFPB-DHzDS was acquired by a D/max-2400 X-ray powder diffractometer (Rigaku, Japan) with Cu Kα radiation (λ==1.54056 Å). Fourier-transform infrared spectra were obtained on a Nicolet Nexus 670 Fourier transform infrared spectrometer (FT-IR, America) using KBr pellets. The scanning electron microscopy (SEM) images were collected on a JSM-6701F field emission scanning electron microscope (JEOL, Japan).

All CEC experiments were performed on a CE instrument assembled by our laboratory with 2600 UV–vis CE detector (CoMetro Technology, Ltd., New York, USA), and the detection wavelength was 226 nm. The data collection and operation system were carried out using a V2008MAX chromatography workstation (VanShine Instrument Co., Ltd., Shanghai, China). The high voltage power supply was obtained from Dong-Wen High Voltage Power Co., Ltd. (Tianjin, China).

Naphthalene (NAP), anthracene (PHE), pyrene (PYR), fluoranthene (FLT), 3-(2,3-epoxy-propoxy)propyltrimethoxysilane (GLYMO), 4-formylphenylboronic acid were purchased from Energy Chemical Co., Ltd. (Shanghai, China). Benzo[b]fluoranthene was purchased from Tokyo Chemical Industry Co., Ltd. (Japan). 1,2-benzo[a]anthracene was purchased from Sigma-Aldrich Trading Co Ltd. (Shanghai, China). Acenaphthene (ANA), fluorene (FLU), anhydrous tetrahydrofuran, dichloromethane, acetonitrile, acetic acid, acetone, methanol and toluene were purchased from Rionlon. Co., Ltd (Tianjin, China). 2,5-bis(3-(ethylthio) propoxy) terephthalohydrazide (DHzDS) was obtained from Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd (Changchun, China). 1,3, 5-tribromobenzene, tetra(triphenylphosphine)palladium, benzophenanthrene (BPH) were purchased from Adamas Reagent, Ltd (Shanghai, China). Thiourea, potassium carbonate and anhydrous magnesium sulfate were obtained from Tianjin Guangfu Co., Ltd. (Tianjin, China). The bare capillaries (75 μm i.d. 200 μm o.d.) were got from Yongnian Photoconductive Fiber Factory (Hebei, China). Ultrapure water was used throughout the experiments.

CEC conditions

When the bare capillary was used for the first time, it was rinsed with anhydrous methanol, ultrapure water, 1 M NaOH (30 min), ultrapure water, 1 M HCl, ultrapure water for 10, 10, 10, 10 and 10 min, respectively. Between two runs, the bare capillary was rinsed with 1 M NaOH, ultrapure water and buffer solution for 2 min, respectively. The coated capillary was rinsed for 5 min with ultrapure water and buffer solution before using. And between two runs, it was rinsed with ultrapure water and buffer solution for 2 min, respectively. The buffer solution was freshly prepared before each running and filtered through a 0.45 μm nylon membrane following by ultrasonic degassing for 2 min. The CEC system were performed at room temperature using a voltage of +20 kV with a height difference 10 cm injection in 3 s. The total length and effective length of the capillary used in the experiment was 60 cm and 47.5 cm, respectively.

Simulation procedures

The simulations of the interactions of 10 PAHs with COF TFPB-DHzDS were conducted by AutoDock 4.2. The crystal structures of the COF TFPB-DHzDS was taken from the references[2]. Molecular structures of 10 PAHs were generated by GaussView 5.0 and their structural optimization were achieved by Gaussian 09 program[3] with density functional theory (DFT, b3lyp/6-31+g(d,p)). The torsion roots of PAHs were detected and rotatable bonds were defined through the aid of AutoDock. 100 runs were performed for each PAHs by Lamarckian genetic algorithm (LGA)[4] to get the most possible conformations of the PAHs interacting with TFPB-DHzDS and the binding energies.

Reference

[1] V.S. Vyas, F. Haase, L. Stegbauer, G. Savasci, F. Podjaski, C. Ochsenfeld, B.V. Lotsch, A tunable azine covalent organic framework platform for visible light-induced hydrogen generation, Nat Commun 6 (2015) 8508.

[2] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, 09, Revision D. 01, Gaussian[J]. Inc.,Wallingford, CT, 2009.

[3] G.M. Morris, D.S. Goodsell, R.S. Halliday, R. Huey, W.E. Hart, R.K. Belew, A.J. Olson, Automated docking using a Lamarckian genetic algorithm and an empirical binding free energy function. J Comput Chem 19 (1998) 16391662.