Supporting Information

Covalent Organic Frameworks-Based Paper Solid Phase Microextraction Combined with Paper Spray Mass Spectrometry for Highly Enhanced Analysis of Tetrabromobisphenol A

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Synthesis of TpBD. TpBD was synthesized according to previous report[1]. 1, 3, 5-triformyl resorcinol (Tp, 63 mg, 0.3 mmol), benzidine (BD, 82.9 mg, 0.45 mmol), 1.5 ml trimethylbenzene, 1.5 ml dioxane and 0.5 ml aqueous solution of 3 M acetic acid were loaded into 10 ml Shrek tube. The mixture was ultrasonic treated for 10 minutes to obtain a uniform dispersion. The tubes were then frozen rapidly in a 77 K liquid N_2 bath and degassed through three refrigeration-pump-melt cycles. After that, the tube was sealed and heated at 120 °C for 3 days. The resulting red sediment is collected by centrifugation or filtration and washed with anhydrous acetone. The collected powder was then washed with anhydrous acetone overnight and vacuum-dried at 180 °C for 24 hours to produce an orange red powder with a separation yield of 75%.

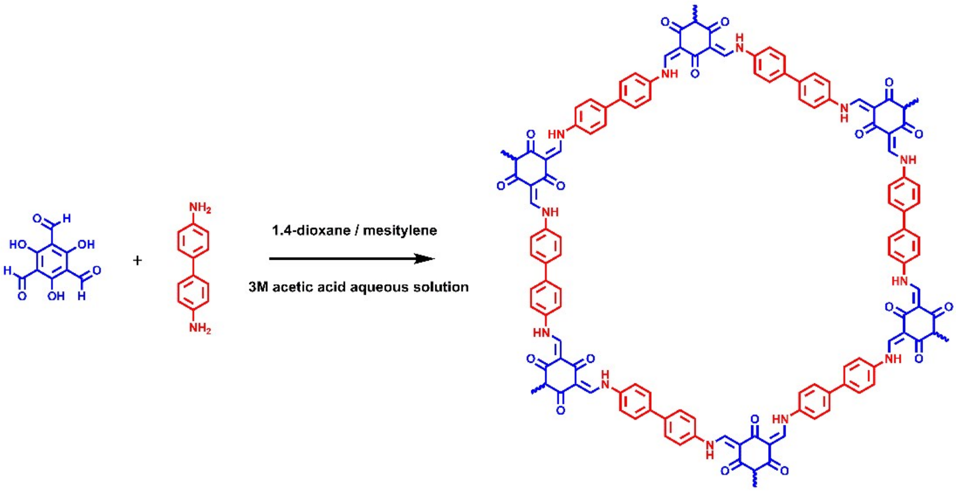

Figure S1. Synthesis process of TpBD.

Characterization of TpBD. As revealed from XRD analysis (Figure S2a), the first and most intense peak corresponding to the (100) reflection plane appeared at ~3.4° (2θ), with other minor peaks at ~5.87° (2θ) and ~27.4° (2θ), they attributed to the (200) and (001) reflection planes, respectively. Peaks at higher 2θ corresponded to the $\pi-\pi$ stacking between the COF layers and could be assigned to the (001) reflection planes. In order to check the thermal stability of TpBD, TGA was performed under a flow of N_2 gas (Figure S2b). It is observed that COF pores are guest free and have almost identical thermal stabilities up to 360 °C. The porosity of TpBD was studied by N_2 adsorption and desorption experiments at 77 K (Figure S2c and S2d). Based on the NLDFT model, it has a narrow pore size distribution centered at 1.2 nm. The Brunauer−Emmett−Teller (BET) surface area is calculated to be 247.8 m^2 g^{-1}. All of these results certified that TpBD is crystalline, porous, and stable, which is vital for further applications.

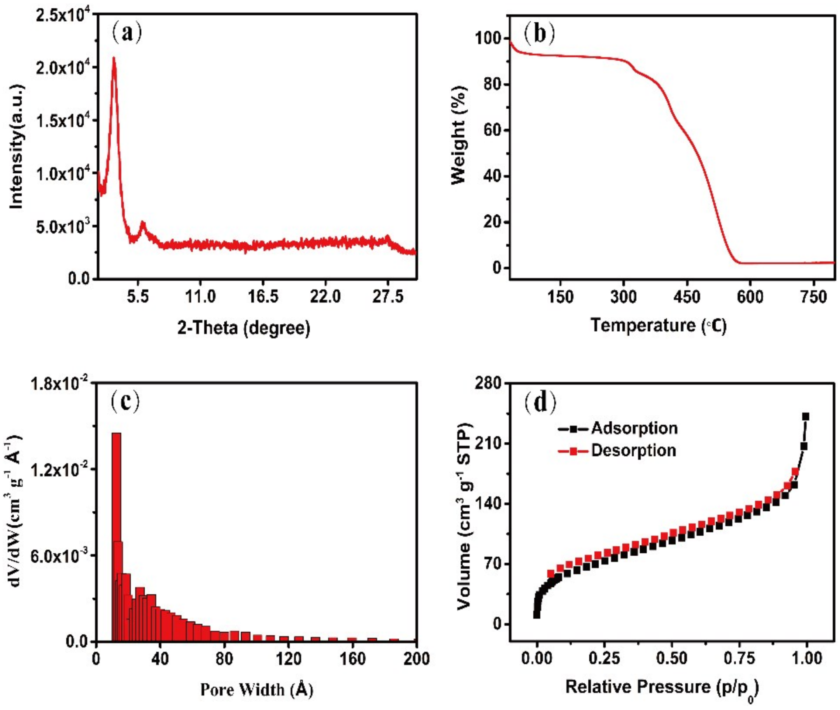

Figure S2. (a) X-ray diffraction (XRD) patterns; (b) TGA curves; (c) Pore size distribution; and (d) Nitrogen adsorption−desorption isotherms of TpBD.

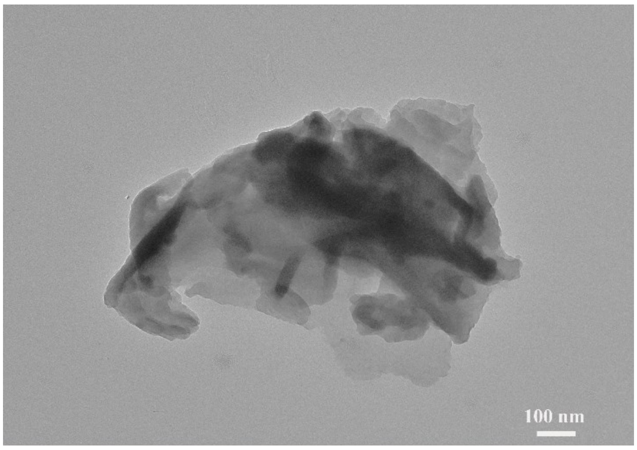

Figure S3. The SEM of TpBD.

Synthesis procedures of internal standard (IS) TBBPA-MHEE. TBBPA-MHEE was prepared based on previous reports[2]. Solution I was obtained by dissolving 168 mg sodium hydroxide in 1.2 mL water. Solution II was obtained by dissolving 1.09 g TBBPA and 16 μL 2-bromoethanol in 5 mL acetone. Then solution I was added dropwise into solution II under vigorous stirring at room temperature. After that, the mixture was diluted with dichloromethane and washed three times with saturated sodium bicarbonate solution and water, respectively. The organic layer was separated and dried with anhydrous $MgSO_4$. After removing the organic solvent, the residue was purified by column chromatography with the eluent (petroleum ether: ethyl acetate=5:1, V: V) to obtain TBBPA-MHEE with a yield of 40% (0.472 g). ^1H NMR (400 MHz, DMSO): δ 9.85, 7.45, 7.38, 4.91, 4.90, 4.88, 3.97, 3.96, 3.94, 3.78, 3.77, 3.76, 3.74, 1.59. ^{13}C NMR (101 MHz, DMSO): δ 151.23, 149.40, 149.08, 143.79, 131.34, 130.80, 117.84, 112.33, 75.18.

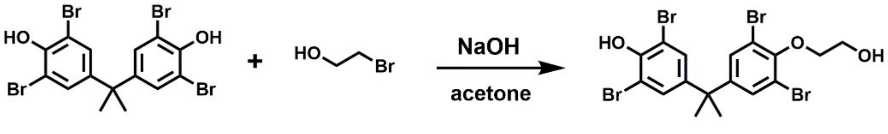

Figure S4. Synthesis route of TBBPA-MHEE.

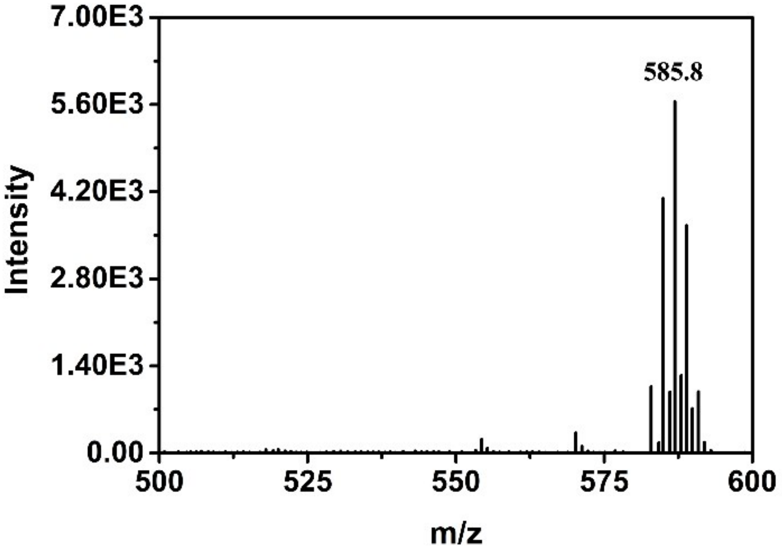

Figure S5. Mass spectrometry of TBBPA-MHEE.

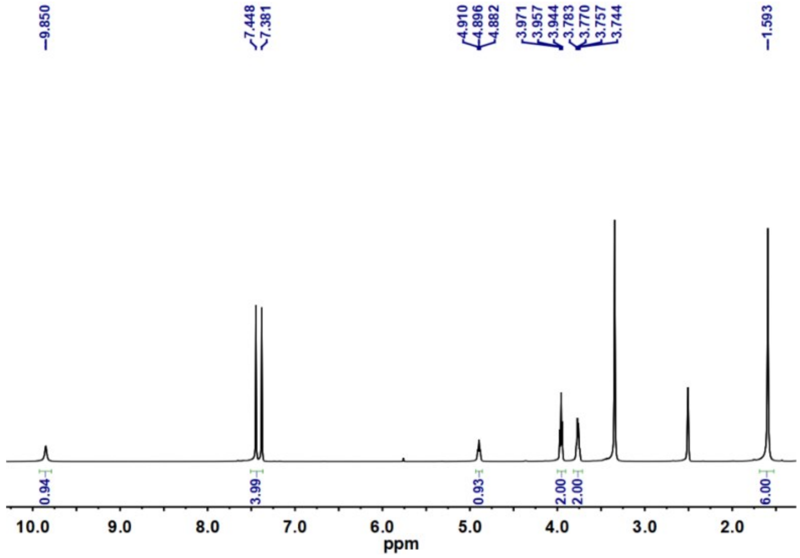

Figure S6. ^{1}H NMR spectrum of TBBPA-MHEE.

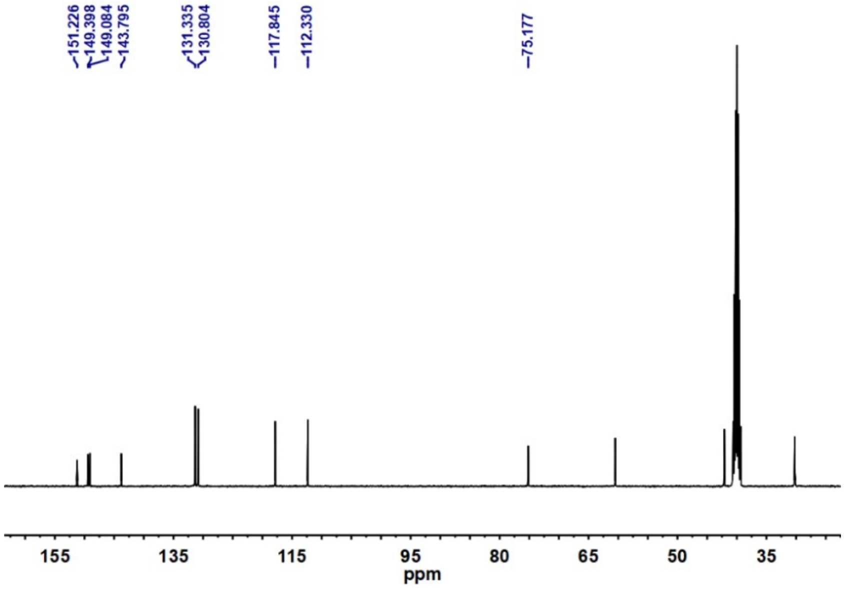

Figure S7. ^{13}C NMR spectrum of TBBPA-MHEE.

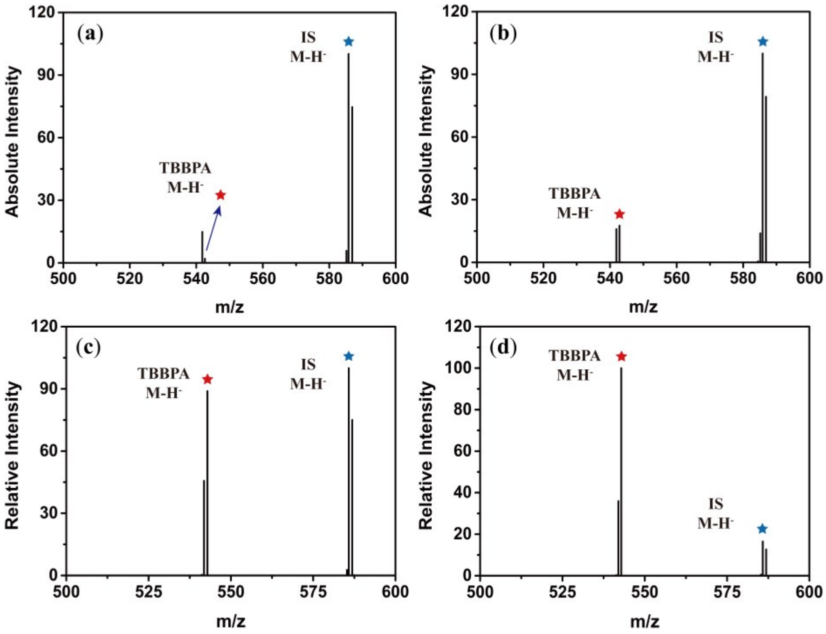

Figure S8. The PS-MS mass spectra of (a) 0 nmol L^{-1} TBBPA; (b) 0.2 μmol L^{-1} TBBPA; (c) 1 μmol L^{-1} TBBPA; (d) 10 μmol L^{-1} TBBPA with 10 μmol L^{-1} TBBPA-MHEE.

Table S1 The comparison between this work and HPLC-MS/MS method.

Method	Linear range (nM)	Added (nM)	Found (nM)	Recovery (%)	RSD (%, n =3)
This work			not detected		
	1-800	50	49.66±2.68	99.27±5.37	5.41
		500	493.71±8.76	98.74±1.75	1.78
HPLC-MS/MS			not detected		
	0.92-772	50	50.06±2.87	100.13±5.73	5.73
		500	503.01±8.29	100.60±1.66	1.65

Table S2.Comparison of the analytical performances of TpBD@Paper-based SPME-PS with reported methods.

Sample preparation	Method	Separation / Detection time	Samples	LOD (ng L^{-1})	LOQ (ng L^{-1})	RSD (%)	Ref
SPME	HPLC-UV	17/10.5	River water, waste water	900	-	5.1	3
SPME	HPLC-ESI MS	30/12	Tap water, effluent	23	59	8.5	4
LLE	HPLC-ICP MS/MS	-/20	Tap water, river water, seawater	120	-	2.0	5
MSPE	HPLC-UV	15/15	Tap water, lake water, rain water, snow water	400	-	-	6
US-DLLME	HPLC-VWD	7/12	Tap water, river water, waste water, urine, fruit juice	130	430	4.3	7
TLC	HPLC-DAD	-/25	Soil	87000[a]	290000[a]	2.06	8
SPME	PS-MS	5/3.5	Tap water, spring water, lake water	164	544	7.12	This work

[a] ng kg^{-1}

SPME: Solid phase microextraction

LLE: liquid-liquid extraction

MSPE: Magnetic solid-phase extraction

US-DLLME: Ultrasound-dispersive liquid-liquid microextraction

HPLC-VWD: High performance liquid chromatography/variable wavelength detection

TLC: Thin-layer chromatography

HPLC-DAD: High performance liquid chromatography-diode array detector

PS-MS: Paper spectrometry mass spectrometry

References

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